An Investigation into the Mechanisms Controlling the Formation of High Density Sludge

by

Christopher James Bullen

Thesis submitted to the University of Wales
for the Doctor of Philosophy

School of Engineering
University of Wales Cardiff

May 2006

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

Summary

One of the legacies of mining is the generation of minewater which can be toxic to the environment and requires treating prior to discharge. This can be treated by either passive or active systems, with the latter being most common for high volume, high load minewaters or those that are difficult to treat. Conventional minewater treatment using pH adjustment can precipitate a large volume of voluminous sludge that is expensive to dispose of. This led to the development of the High Density Sludge (HDS) process in the 1960s, which has now become accepted as the best practical method of treating minewaters whilst minimising the volumes of sludge generated.

The mechanisms controlling the formation of HDS are not fully understood and as a result there are a number of misconceptions adversely affecting the use of the HDS process. The primary objective of the present research was to explore in greater depth the mechanisms controlling HDS formation and hence dispel some of these commonly held misconceptions.

The current understanding of the HDS process was initially established by undertaking a review of information reported in the technical literature. The key operating parameters and concepts were then identified by undertaking a performance review of the 440l/s HDS plant at the former Wheal Jane tin mine in Cornwall, UK. A series of laboratory batch tests and continuous pilot trials were undertaken to assess the importance of these concepts and generate an understanding of the sludge characteristics and properties. The sludge characteristics were investigated by reviewing the sludge settlement (settlement velocity and the ability of the sludge to self compact) and dewatering characteristics. The sludge properties examined were: mineralogy (by X-Ray Diffraction, XRD), morphology (by Scanning Electron Microscopy, SEM, and Transmission Electron Microscopy, TEM) and surface electrical potential (by measuring the zeta potential).

The research has shown that the dominant mechanism for the formation of Type II HDS involves establishing a pH in the Stage I Reactor that gives a negative charge to the recirculated solids. Physical adsorption then ensures heterogeneous nucleation. Control of the pH in the Stage II Reactor ensures removal of the final trace of metals from solution and return of sludge that is capable of achieving the desired pH in the Stage I Reactor. A review of the relevant literature suggests that too high a pH in the Stage I Reactor will favour homogeneous nucleation and hence inhibit HDS formation.

The research has also shown that HDS can be formed using non calcium based alkali reagents and that iron is not required for its generation. Synthetic zinc and manganese minewaters produced HDS with the best settling characteristics. The sludge characterisation showed that there is no requirement for the HDS to be crystalline in nature. The presence of species such as calcium and magnesium cations can 'swamp' the process and slow down the formation of HDS, though they do not prevent its production.

Finally, the research undertaken has shown that the HDS process enhances (by over forty times) the dewatering characteristics of the sludge generated during minewater treatment, the original purpose for which the process was developed.

Declaration

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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This thesis is the result of my own investigations, except where otherwise stated. Other sources are acknowledged by footnotes giving explicit references. A bibliography is appended.

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Acknowledgements

I would like to thank Dr R Coulton, Managing Director, Unipure Europe Ltd, for his assistance in undertaking this work. I am also grateful for the technical assistance given by Jeff Rowlands, Devin Sapsford, Ravi Mitha and Carl Williams from the School of Engineering during the various stages of the work.

The author would also like to thank United Utilities Industrial for the support during the early stages of the research.

I would also like to thank my supervisor, Dr K Williams, for his help, guidance and support throughout the project.

Finally, I would like to thank Non for her patience and understanding during the time it has taken to complete this research.

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1 INTRODUCTION

The historical impact of mining coal and metals is well documented. In the UK alone, there are in excess of 300 discharges from abandoned mines, affecting approximately 700 km of rivers. These discharges can be laden with metals, particulate matter and can be acidic in nature and cause significant input of toxic elements (e.g. iron and other metals) into the natural environment.

Much work has been undertaken in predicting the water quality of the discharges, and with time, the water quality does generally improve. However, the improvement in the water quality can take decades, requiring medium to long-term control and treatment prior to release of the minewater to the watercourse.

The most common active treatment method of minewater employed is 'conventional chemical precipitation' However, this process produces a voluminous sludge that typically has a maximum settled sludge concentration of between 1% and 5% solids, and can be difficult to dewater further. In Canada alone, it was estimated that in 1997, 6.7million m^3 of this low density sludge (LDS) was generated as a result of treating acid minewater through conventional chemical precipitation.

The disposal of this sludge can be costly and long-term storage is uncertain as the metals removed can be released under certain conditions. This has led to the development of the High Density Sludge (HDS) process (Kostenbader *et al.*, 1970). This process, though essentially still a chemical oxidation process, can lead to sludge with different physical (settled solids concentrations of between 15% solids and 35% solids are common) and chemical characteristics. Due to these different physical and chemical properties, the sludge settlement characteristics and dewaterability can be greatly enhanced, as can the sludge stability.

Since the installation of the first full-scale HDS treatment plant at Bethlehem Steel works in the late 1960's, numerous HDS treatment plants have been subsequently installed worldwide. However, though the knowledge of the HDS process as a whole has increased greatly, the detailed scientific understanding of the key parameters has not been reported in the literature. Kostenbader (1970), who undertook the first research on HDS, suggested the key process parameters were:

- Fe (II) to Fe (III) iron ratios in the feed water;

- Ratio of solids recirculated to new solids precipitated;
- Point of alkalinity addition;
- Neutralisation pH; and
- Retention time.

Further developments to the process were undertaken by Bosman (1983), who added the following to the list of key process parameters:

- Retention time in lime/sludge mix tank.
- Peripheral velocity of lime/sludge mix tank mixer impellor.
- Total iron content of the acid minewater.
- Amount of calcium sulphate precipitated from solution.

The work undertaken in this project, and reported in the subsequent chapters, has attempted to move the scientific understanding of the HDS process forward and dispel some misconceptions and contradictory beliefs surrounding the HDS process. The objectives of the project were to:

1 Show that HDS can be formed when using a non calcium based reagent as the alkali reagent.
2 Demonstrate that HDS could be formed by non or low iron feed waters (as with Britannia (Canada) minewater (Section 2.2).
3 Examine the differences in behaviour between bivalent and trivalent metals.
4 Generate HDS from different feed synthetic minewaters and to note the difference in the sludge properties.
5 Review the reported key operating parameters and confirm those which are fundamental to the generation of HDS.

The research was undertaken by reviewing the treatment methods currently used, including the HDS process (Chapter 2). The performance of a full-scale HDS plant (Chapter 4) was reviewed. A set of laboratory batch tests were undertaken to carry out an initial process screening exercise (Chapter 5) prior to a series of continuous pilot plant trials being completed (Chapter 6). The sludge developed during the continuous pilot plant trials was subjected to a series of sludge characterisation tests (Chapter 7) to assist with the development of a greater understanding of the mechanisms involved in the formation of the Type II HDS process (Chapter 8).

The results of the work undertaken are summarised and the final conclusions discussed (Chapter 9). The following outlines each chapter in more detail:

In Chapter 2 minewater generation and treatment is outlined. Discharges of minewater have to comply with strict consent limits (e.g. the consent at Wheal Jane MWTP limits iron to 5 mg/l and manganese to 1 mg/l), necessitating treatment prior to discharge to the environment. Treatment methods are introduced, including the high density sludge process. A by-product of this treatment process is the generation of a waste sludge, which is potentially environmentally damaging and costly to dispose of. The HDS process increases the long-term stability of the sludge, minimises the volume generated and hence reduces the disposal costs (Zinck, 1997).

In Chapter 3 wastewater analysis is discussed. Routine chemical analysis methodologies are outlined as are the sludge characterisation tests undertaken in this research.

In Chapter 4 the Wheal Jane HDS Minewater Treatment Plant (MWTP), UK's largest minewater treatment plant, is introduced. The treatment process selection and installation procedures are outlined, as is the performance of the plant.

In Chapter 5 the batch test methodology is introduced, with the results of the tests undertaken presented. To undertake an initial screening exercise on the use of different alkali reagents (i.e. hydroxides and carbonates of alkali metal or alkali earth metal and magnesium hydroxide are termed as alkali reagents hereon), synthetic Wheal Jane minewater was treated by various alkali reagents. Additionally, synthetic minewater of different metal composition was tested.

In Chapter 6 a series of continuous pilot plant trials were undertaken to confirm that HDS could be formed using sodium hydroxide as the alkali reagent and from minewater without the presence of iron. The sludge characteristics were compared to further the understanding of the HDS process.

In Chapter 7 the sludge generated during the continuous pilot plant trials was subjected to further examination. The results of the further examinations were used in Chapter 8 to help develop an understanding of the mechanisms that contribute to the formation of Type II HDS.

In Chapter 9 the final conclusions are presented.

2 BACKGROUND TO MINEWATER GENERATION AND TREATMENT

2.1 Introduction

The historical impact of mining coal and metals is well documented in the literature (Barnes *et al.*, 1968: Glover, 1983: NRA, 1994: Thomas, 1969: Younger, 1997). In the UK alone there are in excess of 300 discharges from abandoned mines (Younger, 1997), affecting approximately 700 km of rivers (NRA, 1994: Younger, 1997). These discharges can be laden with metalliferous wastes, particulate matter and can be acidic in nature and cause significant input of toxic elements (e.g. iron, zinc, cadmium etc as at Wheal Jane, see Chapter 4 for more detail) into the natural environment.

Much work has been undertaken in predicting the quality of the discharges once mining is stopped (Wood *et al.*, 1999: Younger, 2000), and, with time, the water quality does generally improve following an initial 'first flush'. However, the improvement in the water quality can take decades (Wood *et al.*, 1999), requiring medium to long-term control and treatment prior to release of the minewater to the watercourse.

This chapter summarises the activities in the formation of minewater (commonly known as Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD)), its control and the current treatment methods used. Particular attention is paid to minewaters that contain high metal loads and/or minewaters that are problematic to treat and the most common methods of treating these types of minewaters, including conventional minewater treatment and the high density sludge (HDS) process (an oxidation and chemical precipitation process).

It is worth noting that minewater can be alkaline as well as acidic depending on the mineralogy of the orebody, however acidic minewater will be focused on here.

2.2 Acidic Minewater Generation

The quality of the minewater generated is dependant on the mineralogy of the rock body in the vicinity of the mine. If sulphide minerals, and in particular iron pyrites, are exposed to moisture and oxygen (for oxidation), acidic waters can be formed.

Prior to mining, natural weathering of the exposed rock body can cause minor oxidation near the surface of the orebody. However, due to this occurring over geological time scales, limited activity occurs.

During early shallow mining (prior to deep mine dewatering being available), adits (horizontal tunnels into the mine) were used as a means of lowering the water table and gaining access to the orebody. During the mining process, the orebody was exposed to oxygen and moisture, resulting in the first releases of polluting minewater. This led to the early term "Red River", due to the release of minewater (often containing Fe (III) hydroxide) in to the local watercourses.

During the 18th and 19th centuries, when the lowering of the water table in mines was first possible due to improved dewatering and pumping capacities, deep mining started. This often led to the local groundwater being drawn down significantly. This, coupled with the exposure of large areas of sulphide bearing orebody due to the mining process, caused great potential for acidic minewater to be formed.

When mining stops, and the mine dewatering pumps are switched off, the groundwater levels are allowed to rebound. This allows the rising water to flush the oxidised orebody surfaces and can lead to the release of highly polluting waters to the environment. This process is often termed the 'first flush' (Wood *et al.*, 1999) and can lead to highly contaminated waters. Examples of this are Dalquharran, in Ayrshire, Scotland, where the minewater contained iron concentrations of 1,200 mg/l (Wood *et al.*, 1999) and Ynysarwed, in South Wales, where the iron concentrations exceeded 400 mg/l (Ranson *et al.*, 1997). Probably the most infamous example in the UK is that of the waters released from the Wheal Jane tin mine in Cornwall. In 1992 a release of between 25,000 and 50,000 m^3 of acidic minewater, containing in excess of 5,000 mg/l of dissolved metals (Younger *et al.*, 2005), caused a 25 km plume of contaminated minewater. A more detailed account of Wheal Jane minewater can be found in Chapter 4.

Though a proportion of minewaters do contain high concentrations of iron (i.e. above 100 mg/l), this is not always the case, e.g. Britannia minewater, British Columbia, Canada.

Table 2.1 presents a summary of selected minewaters that contain high metal concentrations and/or high metal loads by exerting an alkali reagent demand.

In addition, the concentrations of dissolved carbon dioxide in the minewater can have implications for the treatment process.

Table 2.1: Typical high metal load minewater and key determinants (average total concentrations)

Mine	Flow m^3/day	pH	Total Concentrations			Daily average total metal load		
			Fe mg/l	Al mg/l	Mn mg/l	Fe kg/day	Al kg/day	Mn kg/day
Wheal Jane (Cornwall, UK) (i)	17,000	3.5	191	20	6	3,247	340	102
Ynysarwed (South Wales) (ii)	2,400	5.8	121	0.3	3.2	290	1	8
Horden (County Durham, UK) (iii)	4,750	6.8	80	0.1	1.2	380	1	6
Brunkunga (South Australia) (iv)	600	2.7	1,270	1,550	90	762	930	54
Parys Mountain (North Wales) (v)	1,000	2.8	565	72	19	565	72	19
Britannia (British Columbia, Canada) (vi)	25,200	3.3	11	30	4.2	277	756	106

References:
(i) Coulton et al., 2003b
(ii) Ranson et al., 1987.
(iii) Coulton et al., 2004b.
(iv) Earth Systems, 2004.
(v) Unipure Europe Limited, 2005.
(vi) Government of British Columbia, 2004.

2.2.1 Minewater Chemistry

As outlined in Section 2.2, the generation of acidic minewater normally requires the exposure of pyrite (FeS_2) to water (H_2O) and oxygen (O_2). The generation of acidic minewater is well documented in the literature (Younger *et al.*, 2002: Skousen, 1995), however these are frequently presented as variations of the following equations (Stumm *et al.*, 1996):

$$FeS_2 + {}^7/_2O_2 + H_2O = 2SO_4^{2-} + Fe^{2+} + 2H^+ \quad \text{(Equation 2.1)}$$

$$Fe^{2+} + {}^1/_4O_2 + H^+ = Fe^{3+} + {}^1/_2H_2O \quad \text{(Equation 2.2)}$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad \text{(Equation 2.3)}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15\,Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad \text{(Equation 2.4)}$$

The first step is the oxidation of sulphide found in the pyrite to sulphate, releasing Fe (II) iron and acidity into the water (Equation 2.1). The Fe (II) iron is oxidised to Fe (III) iron (Equation 2.2), which is then precipitated as Fe (III) hydroxide

(Equation 2.3) releasing more acidity. Any Fe (III) left in solution can oxidise additional pyrite, releasing more acidity and Fe (II) iron (Equation 2.4). Equations 2.2 and 2.4 can combine to form a very rapid and cyclic process that can produce an acid minewater with high levels of acidity and high concentrations of heavy metals (Stumm *et al.*, 1996).

Oxidation of Fe (II) to Fe (III) may be rate limiting in low pH waters. However, autotrophic bacteria present, such as *Acidithiobacillus ferroxidans,* can catalyse the process by oxidising the Fe (II) iron to Fe (III) iron and increasing the rate of acidity production (Singer *et al.*, 1970).

Acidity is defined as the minewater's capacity to react with a strong base to a predetermined pH value and is based on the total acidity of the minewater, i.e. proton (from strong and weak acids) and mineral acidity (from metal ions). Alkalinity is defined as the minewater's capacity to react with a strong acid to a predetermined pH and is made up of the carbonate, bicarbonate and hydroxides.

2.3 UK Legislative Requirements

In the UK, discharges from mines (active and abandoned) are controlled by by the Environment Agency enforcing UK legislation, which is directed by European Directives.

The Control of Pollution Act 1974 (COPAC 1974) was the first piece of modern legislation controlling discharges from mines. COPAC 1974 was superseded by the Water Act 1989, which in turn was superseded by the Water Resources Act 1991 (WRA 1991). The WRA 1991 controlled the discharges from active mines but excluded discharges from abandoned mines, Section 89 (3) "permitted polluted waters to flow from abandoned mines". This exemption was removed in the Environment Act 1995 (EA 1995) for mines closed after 31 December 1999. The requirement for the mine owner to give six months notice along with water quality, flow information and mine layout to the Environment Agency, was enacted in The Mines (Notice of Abandonment) Regulation 1998. The UK Coal Authority has taken on the responsibility for discharges from mines closed before 1999.

The European Union's aim is to prevent a deterioration of any watercourse and ensuring all watercourses are of a "good status". The European Union Water Framework Directive (WFD), adopted in September 2000 and enforced on 22nd

December 2000, sets out the means with which discharges from mining activities should meet the European Union's aims. It is up to the national authorities to achieve these targets by ensuring the legislative requirements of the WFD are met by each country's own legislation.

Under the European Water Frame Work Directive, the UK Government, through the Environment Agency (EA), sets water quality standards for watercourses in the UK. Through the water quality standards, the discharge standards to be achieved from mines (active and abandoned) are controlled.

2.4 Minewater Prevention and Control

If generation of acidic minewater is predicted, preventative and control measures should be investigated to limit the generation and release of acidic minewater. Theoretically, by controlling the transfer of water and air (oxygen) to the sulphide bearing orebody, the generation of acid minewaters can be prevented or at least controlled. However, it is often extremely difficult to prevent the formation of acidic minewater due to the complex nature of historical mine workings, tailings and waste disposal sites. Measures should therefore be taken to minimise and control the generation of acid minewater. Techniques employed include: waste removal, surface coverings, water diversions, infiltration control, re-vegetation, carbonate surface covers, and water table elevation controls, e.g. Glennwhite Watershed, Blair County, Pensylvavnnia, US (www.altoonawater.com). By minimising the volume of minewater released and limiting the oxidation processes, the eventual volume and pollutant load in the minewater released can be controlled, and hence reduce the size of treatment facility that will be required.

2.5 Minewater Treatment

Once the volume and pollutant load of the minewater have been established, the choice of treatment technology and method that will be required prior to discharge of the treated minewater to the environment has to be made. Selection of treatment process is normally based on technical and economic considerations. When considering the technical aspects, maturity and robustness of the treatment process, and ability to achieve the required treated water quality, have to be taken into account. With regard to economic considerations, the whole life costs of the project have to be calculated, including capital costs, operational costs and

decommissioning costs (Coulton *et al.*, 2003a).

In principle, all minewater can be treated to drinking water standard (e.g. Horseshoe Curve, Altoona Pennsylvania, US, (Dempsey *et al.*, 1993)), however, this is likely to have great cost and may not be required except in extreme cases.

The primary aims of the minewater treatment are to remove any metals and neutralise any acidity (Brown *et al.*, 2002). The removal of any solid matter from the effluent is a requirement in order to limit any visual impacts caused by the discharge.

In general, the treatment of minewater can be broken down into two categories:

- Active Treatment (which requires the input of resources, including power, chemicals and routine operational activities); and
- Passive Treatment (which is designed to require very limited or no input of resources).

Depending on the discharge standard required, land availability, if the minewater is net acidic or net alkaline and the metal load (metal concentration x minewater flow), either passive or active treatment systems can be used. Figure 2.1 presents the choice of treatment system to be used according to the minewater flow and metal concentration.

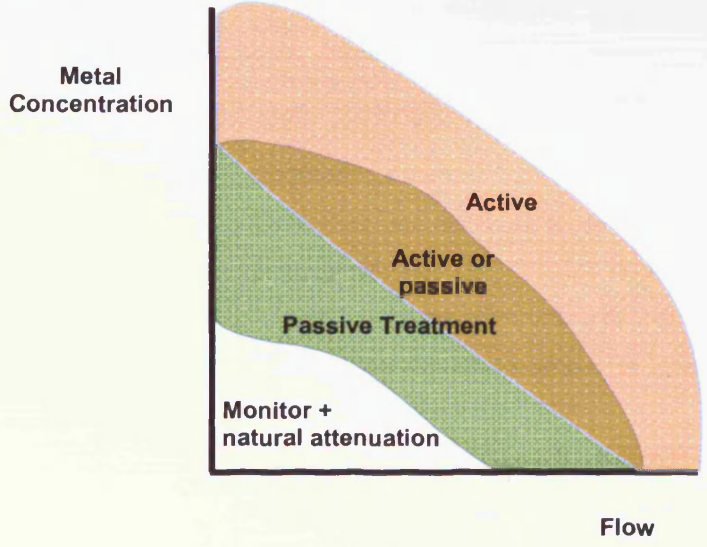


Figure 2.1: Treatment system used according to minewater flow and metal concentration (Coulton, 2004)

Where the metal load is low, use of passive treatment systems are both technically and economically viable (Coulton *et al.*, 2003a). However, as the metal load increases, problematic minewaters are to be treated, or a very high quality discharge water quality is required, use of active treatment systems is preferred.

2.5.1 Passive Treatment Systems

The European Union's PIRAMID R&D project (www.piramid.org) definition of a passive system is:

"Passive treatment is the deliberate improvement of water quality using only naturally-available energy sources (e.g. gravity, microbial metabolic energy, photosynthesis), in systems which require only infrequent (albeit regular) maintenance in order to operate effectively over the system design life."

Therefore, passive systems use natural resources to enhance naturally occurring chemical and biological processes.

The current methods used for passive minewater treatment in the UK are presented in Table 2.2 and are described in the literature (Younger, 2000b).

Table 2.2: Current UK passive minewater treatment systems (Younger, 2000b)

Type		Description
1	Aerobic	Surface flow wetlands, which are often termed "reed beds" in the UK.
2	Anaerobic	Compost wetlands with significant flow.
3	Mixed compost / limestone systems	With predominantly subsurface flow. These systems were originally labelled "SAPS" (Successive Alkalinity Producing Systems) by their originators. The label "SAPS" remains popular in the UK. These have recently been referred to as "RAPS" systems (Reducing and Alkalinity Producing Systems).
4	Barriers	Subsurface reactive barriers to treat acidic, metalliferous ground waters.
5	Closed-Systems	Closed-system limestone dissolution systems for zinc removal from alkaline waters.
6	Roughing filters	Used for the aerobic treatment of net-alkaline ferruginous minewater where limited land availability precludes a surface wetland.

It can be seen, from the advantages and disadvantages of passive systems listed in Table 2.3 (Younger *et al.*, 2002a), that where minewater discharges are of high volume and highly metalliferous, the use of active treatment systems are preferable to passive systems.

Table 2.3: Passive treatment systems: Advantages and disadvantages (Younger *et al.*, 2002a)

Advantages	Disadvantages
Low operating costs, and usually low capital costs (at least for small-to medium-sized minewater discharges)	Passive treatment technology is still relatively new, and hence reliable expertise is still scarce
Use non-hazardous materials	Because day-to-day intervention in treatment processes is precluded, precise control of treatment effluent quality is not feasible
If suitably designed and well-constructed, passive systems can work for long periods of time unattended	A large land-take is likely to be necessary for high-flow and/or highly contaminated discharges
Passive systems can often be directly integrated with surrounding ecosystems	Relatively high capital (construction) costs
In many cases appearance is more pleasant than active treatment systems	

2.5.2 Active Treatment Systems

Active minewater treatment systems are used where minewaters are net acidic, difficult to treat passively, are high in metal load, land availability is in short supply or the treatment scheme is of a temporary nature (Coulton *et al.*, 2005). Active treatment of minewater requires the input of resources, be they chemical, power or human. A suitable definition is (Younger *et al.*, 2002):

"Active treatment is the improvement of water quality by methods which require ongoing inputs of artificial energy and/or (bio) chemical reagents."

The active treatment technologies can be summarised as follows (Brown *et al.*, 2002; Younger *et al.*, 2002):

- Pump only,
- Oxidation and chemical precipitation,

- Biology-based treatments (including sulphidisation),
- Ion exchange and sorption treatments,
- Membrane process,
- Electrochemical treatment,
- Other treatment processes.

Detailed explanations of active treatment methods used in minewater treatment can be found in the literature (summarised in Brown *et al.*, 2002; Younger *et al.*, 2002), and is outside the area of this present research. However the 'oxidation and chemical precipitation process' is presented in further detail below.

2.6 Explanation of Oxidation and Chemical Precipitation

The processes involved in treating acid minewater by 'oxidation and chemical precipitation' (a generic name given to the processes involved) are well documented in the literature (Vachon *et al.* 1987; Zinck *et al.*, 2000), and are summarised below.

The solubility of most metals in solution (including minewater) is dependent on the pH of the solution. In general, as the pH of the solution increases, the concentration of the metals in solution decreases. Adding an acid or alkali will change the pH of the solution and will affect the solubility of the metal, and hence, increase or decrease the concentrations of metals in solution. Oxidising certain metals (e.g. Fe (II) to Fe (III)) can also make the metals less soluble and produces a more stable precipitate (Kostenbader *et al.*, 1970). Separating the metal precipitate from the solution by gravity settlement can then produce good quality treated water. However, the precipitates are often small in particle size and require coagulation or flocculation to aid settlement. This oxidation (if required, e.g. when iron is present) and chemical precipitation process is the most common form of heavy metal removal (Eckenfelder, 2000). However, the choice of how and which alkali reagent is used can affect the volume of precipitate generated that will require subsequent disposal.

Historically, the most common method to treat acid minewater was to pump the minewater directly to a tailings dam (if available) for co-precipitation with tailings from the processing mill, shown in Figure 2.2, or for using the tailings dam as a settlement device, as was the case with Wheal Jane minewater (Cornwall, UK)

before 2000 (Chapter 4). This treatment method has become known as the "Conventional Precipitation Process" (Kuyucak, 2001; Coulton *et al.*, 2005; Kostenbader *et al.*, 1970; Keefer *et al.*, 1983; Bosman, 1974). Initially, calcium hydroxide ($Ca(OH)_2$) was used as the alkali reagent to raise the pH and precipitate the metals out of solution, with flocculants occasionally used to aid settlement and clarification.

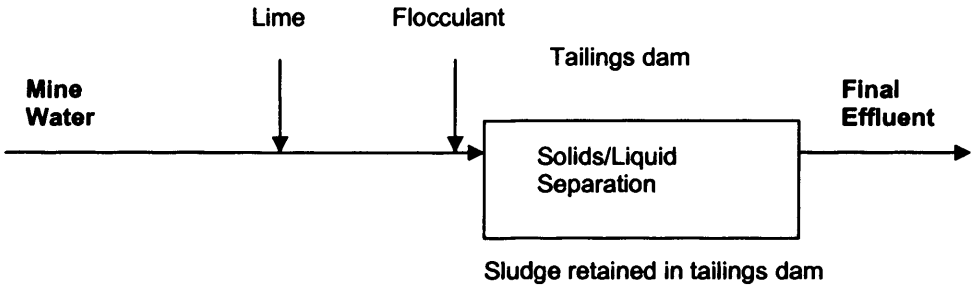


Figure 2.2: Conventional acid minewater precipitation plant (using tailings lagoons)

When tighter process control is required, and/or a tailing dam is unavailable, reaction vessels and settlement tanks are used, as shown in Figure 2.3. In this case, air is often introduced to help oxidation of Fe (II) to Fe (III) iron. Depending on the alkali reagent used, sludge is removed from the bottom of the clarifier at between 3 % solids (w/w), when sodium hydroxide is used, and 5% (w/w), when calcium hydroxide is used, (Kostenbader, 1970; Vachon *et al.*, 1987; Aubé *et al.*, 1999) and can be voluminous in nature (Kostenbader, 1970; Aubé *et al.*, 1999).

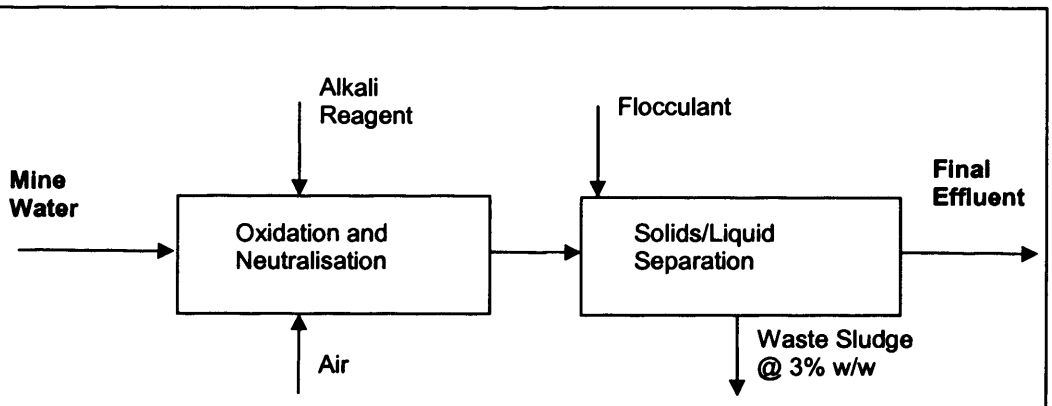


Figure 2.3: Conventional acid minewater precipitation plant (using reaction vessels)

As outlined in section 2.5.3, metals are removed from solution by addition of an alkali reagent. The optimum pH required for minimum solubility for each metal

varies with the metal species and the alkali reagent used. Presented in Figure 2.4 are the solubility curves for common metal hydroxides. If more than one metal is to be removed, a multi-stage system is required or use of a single pH that will enable all target metals to be removed to discharge standards. The alkali reagent used also affects the solubility of the metal, as presented in Table 2.4, with metal sulphides producing a lower metal solubility compared to hydroxides.

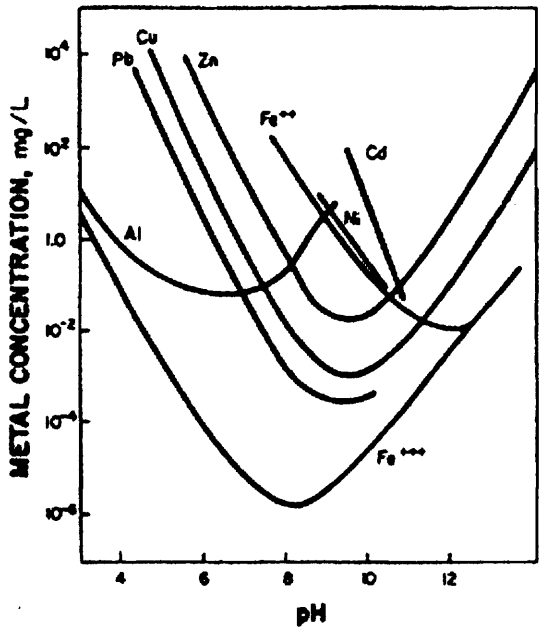


Figure 2.4: Solubility of metal hydroxides (MEND, 1994)

Swindley (1999) investigated removing metal complexes from solution as metal hydroxides. This work showed that the actual solubility of metal ions and the minimum pH for maximum precipitation varies according to the mix of metal ions present in the solution.

Typically, four alkali reagents (i.e. hydroxides and carbonates of alkali metal or alkali earth metal and including magnesium hydroxide and termed alkali reagents hereon), have been used for treatment of acidic minewater: calcium carbonate (limestone), calcium hydroxide (hydrated lime), sodium carbonate (soda ash or briquettes), and sodium hydroxide (caustic soda) (Skousen *et al.*, 1993; Coulton *et al.*, 2003a; Brown *et al.*, 2002; Zinck *et al.*, 2005). Table 2.5 presents a full list of chemicals used in treatment of minewater.

Table 2.4: Theoretical solubilities of hydroxides, sulphides and carbonates of heavy metals in pure water (Lanouette, 1977; US Army, 2001)

Metal		Solubility of metal ion (mg/l)		
		As Hydroxide	As Sulphide	As Carbonate
Cadmium	Cd^{2+}	2.3×10^{-5}	6.7×10^{-10}	1.0×10^{-4}
Chromium	Cr^{3+}	8.4×10^{-4}	No precipitate	-
Cobalt	Co^{2+}	2.2×10^{-1}	1.0×10^{-8}	-
Copper	Cu^{2+}	2.2×10^{-2}	5.8×10^{-18}	-
Iron	Fe^{2+}	8.9×10^{-1}	3.4×10^{-5}	-
Lead	Pb^{2+}	2.1	3.8×10^{-9}	7.0×10^{-3}
Manganese	Mn^{2+}	1.2	2.1×10^{-3}	-
Mercury	Hg^{2+}	3.9×10^{-4}	9.0×10^{-20}	3.9×10^{-2}
Nickel	Ni^{2+}	6.9×10^{-3}	6.9×10^{-8}	1.9×10^{-1}
Silver	Ag^{+}	13.3	7.4×10^{-12}	2.1×10^{-1}
Tin	Sn^{2+}	1.1×10^{-4}	3.8×10^{-8}	-
Zinc	Zn^{2+}	1.1	2.3×10^{-7}	7.0×10^{-4}

Table 2.5: Chemicals used in neutralising minewater (Skousen *et al.*, 1993)

Chemical Name	Chemical formula	Comments
Calcium oxide (quick lime, caustic lime)	CaO	Very reactive, needs metering equipment
Calcium carbonate (limestone)	$CaCO_3$	Used most successfully in anaerobic situations
Calcium magnesium carbonate (dolomite)	$(Ca.Mg)CO_3$	Similar to limestone, less reactive
Calcium hydroxide (hydrated lime)	$Ca(OH)_2$	Requires extensive mixing
Sodium hydroxide (caustic soda)	NaOH	Very soluble, available in solid form (drums or briquettes)
Sodium carbonate (soda ash)	Na_2CO_3	Usually in briquette form, used for remote locations
Potassium hydroxide	KOH	Similar to sodium hydroxide
Magnesium oxide (magna lime)	MgO	Similar to calcium oxide
Magnesium hydroxide	$Mg(OH)_2$	Similar to calcium hydroxide
Ammonia	NH_3 or NH_4OH	Reactive and soluble, can be supplied as aqueous ammonia
Kiln dust	$CaO,Ca(OH)_2$	Waste product of cement industry, contains lime, various other constituents

The choice of chemical used is based on the rate and degree of pH increase, solubility in water, handling and cost of reagent. The amount of alkali reagent

required to precipitate out the metals from solution is usually greater than that predicted stoichiometrically and is controlled by such things as; rate of reaction, size of reaction vessels, and concentration of other elements (e.g. sulphate and carbon dioxide) that are present in the minewater. Table 2.6 summaries the theoretical doses and costs for commonly used alkali reagents.

Table 2.6: Commonly used alkali reagents, theoretical doses and costs (Coulton *et al.*, 2003a)

Reagent		Unit Cost (£/tonne)	Theoretical consumption kg per kg Fe		Actual consumption kg per kg Fe		
			Dose	Cost	Efficiency	Dose	Cost
Calcium Oxide	CaO	100	1.00	10p	65%	1.54	15p
Calcium Hydroxide	$Ca(OH)_2$	100	1.33	13p	65%	2.05	21p
Magnesia	MgO	220	0.72	16p	80%	0.9	20p
Magnesium hydroxide	$Mg(OH)_2$	260	1.04	27p	80%	1.3	34p
Sodium hydroxide	NaOH	260	1.433	37p	95%	1.50	39p
Sodium Carbonate	Na_2CO_3	150	1.89	28p	95%	2.00	30p

Typically, the choice of alkali reagent used is made in terms of calcium or sodium and hydroxide or carbonates.

2.6.1 Calcium vs. Sodium Alkalis

As the solubility of calcium products is lower than that of sodium products the rate of pH change is slower for the calcium products compared to sodium products. The rate of mixing and aeration greatly affects the use of calcium carbonate, calcium hydroxide and sodium carbonate. A comparison of calcium products compared to sodium products is presented in Table 2.7. Calcium costs are generally lower than sodium products and the cost savings when using calcium products compared to sodium products usually means that calcium products are used for treating high flow and high metal loadings whilst sodium products are used where there are low flows and or low metals loadings (due to the reduced capital cost of sodium dosing equipment). A detailed cost comparison of alkali reagents to be used is available in the literature (Skousen *et al.*, 1993).

If sulphate is present in high enough concentrations in the minewater, gypsum can

be formed when calcium products are used. Calcium products can also lead to the formation of calcium carbonate if carbon dioxide is present in the minewater. The generation of both gypsum and calcium carbonate affects the efficiency (ratio of theoretical dose to actual dose) of the alkali reagent, and can also lead to an increase in solids productions and scaling in the minewater treatment plant.

Table 2.7: Factors influencing selection of calcium or sodium compounds for minewater treatment (modified Skousen, 1988)

Factor	Calcium	Sodium
Solubility	Slow	Fast
Application	Requires mixing	Diffuses well
Hardness	High	Low
Gypsum formation	Yes	No
Calcium carbonate formation	Yes	No
High TSS or clay particles	Helps settle clay	Disperses clay particles, and keeps clay in suspension
Chemical cost	Lower	Higher
Health and Safety issues	Lower	Higher
Installation and maintenance costs	High	Low

2.6.2 Carbonate vs. Hydroxide Alkali reagents

The choice between carbonate and hydroxide alkali reagents is generally made on the levels of acidity in the water. If there are low levels of acidity, carbonate alkali reagents can raise the pH to 12 (Skousen *et al.*, 1990). However, if there are high levels of acidity in the minewater, carbonate compounds can only raise the pH to 8.5 to 9.0 (Brown *et al.*, 2002; Skousen *et al.*, 1990). Therefore, if the pH needs to be raised above 9.0, e.g. when there is a need to remove manganese, hydroxide compounds, which can raise the pH up to 12.0, are required. Therefore, depending on the metal species present in the minewater (and their concentrations), the most suitable alkali reagent can be chosen. It is worth noting that, when carbonate is added, e.g. as sodium carbonate ($Na_2^+CO_3^{2-}$), $2H^+$ are removed from the water to keep the equilibrium, see Equations 2.5 to 2.7.

$$2H^+ + Na_2CO_3 = 2Na^+ + 2H_2O + CO_2 \quad \text{(Equation 2.5)}$$

$$M^{2+} + Na_2CO_3 + H_2O = 6Na^+ + M(OH)_2 + CO_2 \quad \text{(Equation 2.6)}$$

$$2M^{3+} + 3Na_2CO^3 + 3H_2O = 6Na^+ + 2M(OH)_3 + 3CO_2 \quad \text{(Equation 2.7)}$$

2.6.3 Metal Ion Hydrolysis and Other Key Reactions

Depending on the metal ions present and the alkali reagent used, different precipitates are formed. Presented in Table 2.8 are the simplistic theoretical precipitates of common metal ions present in minewater. Table 2.8 also presents the alkalinity equivalents for each of the reactions. In general terms, the precipitates from minewater that are dominated by iron are termed as amorphous Fe (III) hydroxides (Georgaki et al., 2004). However, in reality more complex Fe (III) oxy-hydroxides (Dempsey *et al.*, 2001; Lee et al., 2002) are formed.

Table 2.8: Metal ion hydrolysis (Younger *et al.*, 2002, Baes *et al.*, 1976)

Metal ion and other reactions	Equivalents of Alkalinity for a proton condition of pH = 5.64
Aluminium hydrolysis (i) $Al^{3+} + 3H_2O = Al(OH)_3(s) + 3H^+$	-3
Fe (II) Oxidation and Fe (III) Hydrolysis (i) $Fe^{2+} + ¼O_2(aq) + 2½H_2O \rightarrow Fe(OH)_3$ $Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+$	-2 -3
Manganese Oxidation and Hydrolysis (i) $Mn^{2+} + ¼O_2(aq) + 1½H_2O \rightarrow MnOOH(s) + 2H^+$ $Mn^{2+} + ½O_2(aq) + H_2O \rightarrow MnO_2(s) + 2H^+$	-2 -2
Zinc Hydrolysis (ii) $Zn^{2+} + 2H_2O = Zn(OH)_2(s) + 2H^+$	-2
Dissociation of water (i) $H_2O = OH^- + H^+$	0
Carbonate Ion (i) $HCO_3^- = CO_3^{2-} + H^+$	2
Bicarbonate Ion (i) $H_2CO_3 = HCO_3^- + H^+$	1

Note
(i) Younger *et al.*, 2002
(ii) Baes *et al.*, 1976

Depending on the reduction-oxidation potential (termed redox potential in this thesis), pH, oxidation rates and water characteristics (i.e. the environmental conditions), the amorphous sludge commonly precipitated during conventional active minewater treatment is ferrihydrite (Lee *et al.*, 2002; Jambor *et al.*, 1998;

Georgaki *et al.*, 2004; Cornell *et al.*, 2003). If the iron present in minewater is precipitated rapidly (homogeneous nucleation) at pH above 7 at ambient temperatures, '2-line' ferrihydrite is formed (Georgaki *et al.*, 2004; Jambor *et al.*, 1998; Lee *et al.*, 2002) and if the iron is removed at higher temperatures with a lower pH (Lee *et al.* 2002; Bigham *et al.*, 1996), '6-line' ferrihydrite will be formed. Figure 2.5 presents observed X-Ray diffractograms of '2-line' and '6-line' iron precipitates and appear to be amorphous, however this is inaccurate as ferrihydrite exists as nano-crystals less than 10 nm in size (Cornell *et al.*, 2003; Murad, 2004)).

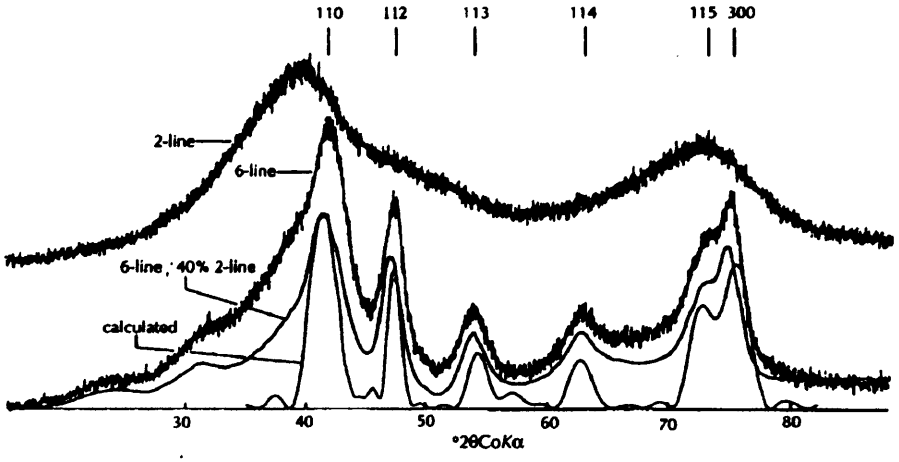


Figure 2.5: Observed 2-line and 6-line ferrihydrite XRD traces, (plus smoothed trace for 6-line with 40% 2-line ferrihydrite subtracted, and pattern calculated assuming 40-Å-size crystals) (Jambor *et al.*, 1998)

Due to ferrihydrite's initial form, i.e. unstructured in nature, very large surface area (typically 200 m^2/g Georgaki *et al.*, 2004; Cornell, 2003) and chemical activity, ferrihydrite can adsorb large quantities of anions, cations and organic species (Georgaki *et al.*, 2004) and assist with the removal of metals from minewater.

If ferrihydrite is not stabilised, with certain environmental conditions and/or time, the sludge can become crystalline in nature (Cornell *et al.*, 2003) and under certain conditions form hematite. Presented in Figure 2.6 (Schwertmann *et al.*, 2000) is one schematic representation of formation and transformation pathways for common iron oxides, together with the approximate transformation conditions.

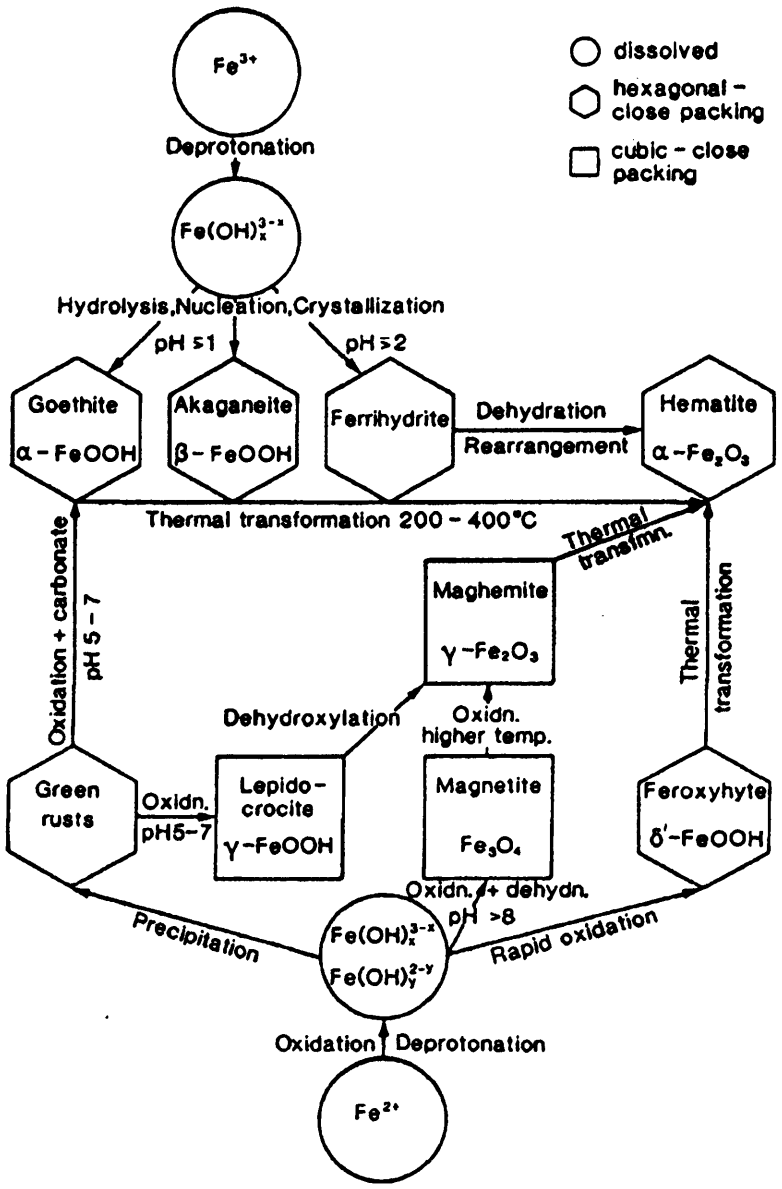


Figure 2.6: Schematic of formation of common iron oxides (Schwertmann *et al.*, 2000)

2.6.4 Sludge Disposal and the High Density Sludge Process

Due to the sludge produced from conventional chemical precipitation plants being voluminous in nature and with a maximum concentration of 5% solids (w/w) (Dempsey *et al.*, 2001), the volume of sludge generated can be high. This sludge can also be difficult to dewater (Vachon *et al.*, 1987; Dempsey *et al.*, 2001), leading to substantial costs for disposal (Kostenbader *et al.*, 1970; Bosman, 1974; Zinick *et al.*, 2000). In 1997, it was estimated that in Canada alone, 6.7 million m^3/year of lime treatment sludge was produced (Zinck *et al.*, 2000).

Understanding the characteristics and stability of the sludge is critical to ensure the long-term disposal is secure and robust. Work has been undertaken (Vachon *et al.*, 1987; Watzlaf *et al.*, 1990; Aubé *et al.*, 1999; Zinck, 1997) where different

treatment conditions and processes were looked at and how they impacted on such things as sludge morphology, mineralogy, composition, particle size, percent solids and the leachability of the sludge. The leachability is a key indicator, as this has an impact on the disposal location and method, with the research indicating that the more crystalline the sludge, the more stable the sludge, resulting in less metals being able to be leached out of the sludge (Zinck, 1997; Aubé *et al.*, 1999).

A considerable amount of work has been undertaken on investigating possible uses for the sludge generated during treatment of acid minewater and minewater in general. These include, pigments (Hedin, 2003), cement fillers (Dudeney, 2005), coagulants (Keefer *et al.*, 1983; Dudeney, 2005), artificial top-soil (Dudeney, 2005; Dudeney *et al.*, 2004), phosphate removal (Heal *et al.*, 2003), and engineering fill (Dudeney, 2005). However, further work is required in this area of research and development to ensure a commercially viable product is developed.

During the late 1960s and early 1970's the High Density Sludge (HDS) process was developed as a means of producing a sludge of much higher settled solids concentration (between 15% and 35% solids (w/w) were reported by Kostenbader *et al.*, 1970). The HDS process is reported to improve the sludge settling and dewatering characteristics (Vachon *et al.*, 1987; Zinck *et al.*, 2000; Aubé *et al.*, 1997; Bosman, 1974; Bosman, 1983; Zinck, 1997)..

The HDS process, as first developed by Bethlehem Steel Corporation (BSC) (Kostenbader *et al.*, 1970), comprises a modification to the conventional precipitation plant. This modification consists of recirculating the settled sludge to a lime mixing tank where the sludge is mixed with lime prior to the mix being added to the reactor to neutralise the acid minewater. (A detailed explanation of the High Density Sludge process can be found in Section 2.8).

2.7 Whole Life Costs: Conventional Treatment vs. HDS

The reduction of the sludge volume produced can reduce the operational costs of a minewater treatment plant substantially. The extra capital costs required to construct a HDS plant are often recouped when treating a highly metalliferous minewater of high volume. Figure 2.7 (Coulton *et al.*, 2003a) suggests that once an annual metal load in excess of 150 tonnes/year is to be treated, a HDS plant is financially viable. Therefore, once a minewater metal load of 150 tonnes/year is

exceeded, the use of the High Density Sludge process becomes commercially viable.

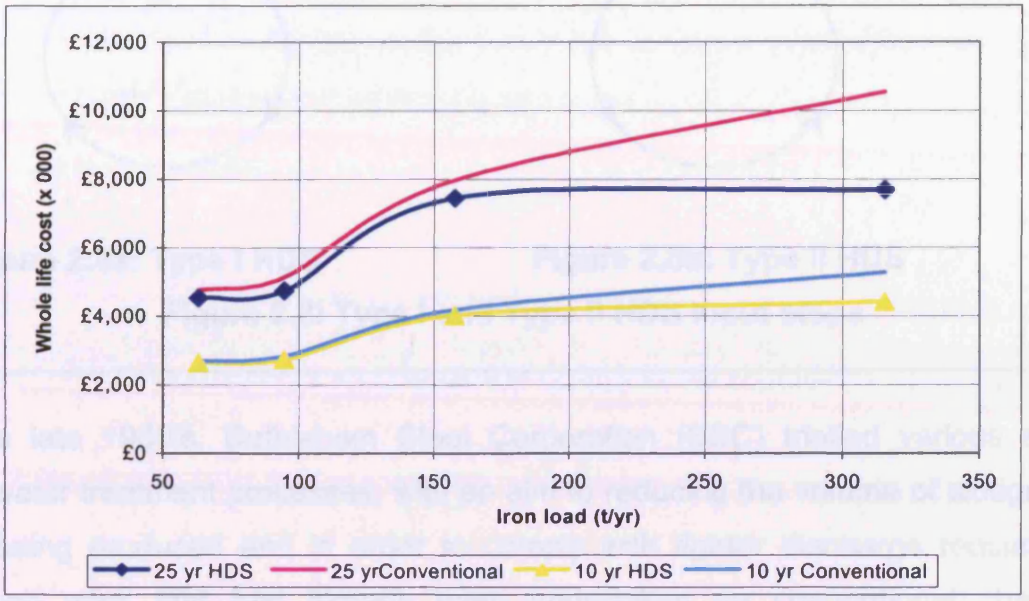
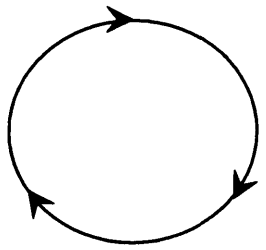


Figure 2.7: Comparison of 10 year and 25 year whole life costs for active treatment plants (Coulton *et al.*, 2003a)

2.8 The development of the Type I HDS process at Bethlehem Steel Corporation

High density sludge (HDS) can be formed by mixing the recirculated sludge with either the alkali reagent, prior to introducing the minewater (Type I), or with the minewater, prior to adding the alkali reagent (Type II), as presented by the author in Figure 2.8. Starting at Step 1 in Figure 2.8a, if a clockwise motion is followed, Type I HDS is formed. By following an anticlockwise motion around the circle, Figure 2.8b, Type II HDS is formed. If the cycle is started at step 2 going clockwise, or step 3 going anticlockwise, conventional chemically precipitated sludge is formed.

The first recorded use of the HDS process was in 1965 for the treatment of a pickle liquor and a steel mill cold reduction waste stream (Dempsey, 1993). The Densator unit, manufactured by Infilco, produced a Fe (II) hydroxide sludge with a solids concentration of in excess of 10% w/v. However, there is little information as to how the units worked. The city of Mankato, Minnesota still uses two Densators in the treatment and supply of water to the public.



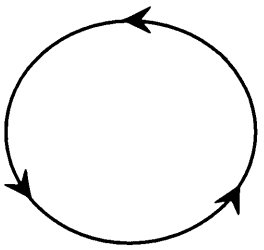


Figure 2.8a: Type I HDS **Figure 2.8b: Type II HDS**

Figure 2.8: Type I and Type II HDS input steps

In the late 1960's, Bethlehem Steel Corporation (BSC) trialled various active minewater treatment processes, with an aim to reducing the volume of sludge that was being produced and in order to comply with tighter discharge regulations. Through work that had already been undertaken on conventional chemical precipitation processes, BSC developed the first minewater High Density Sludge (HDS) process (Kostenbader *et al.*, 1970). (Earlier work undertaken by Cywin *et al.* (1970) and Gaughan *et al.* (1968) furthered the understanding of acidic water treatment prior to the work undertaken by Kostenbader *et al.*, 1970.)

The BSC HDS process is based around a Type I HDS system, with the US patent application filed on 19th April 1971 (Kostenbader, 1971) and awarded on the 12th June 1973. The process was invented for the treatment of acidic waters containing metals, and specifically acid mine drainage and diluted pickle liquor.

The pH of the minewater is raised to between 7.0 and 9.0 in Reactor 1, as shown in Figure 2.9, by using a lime/sludge mix. Air is also introduced to ensure all Fe (II) present is oxidised to Fe (III). In Reactor 1 (retention time between 5 and 20 minutes) a high proportion of the dissolved metals present are removed from solution. The resultant sludge/ liquid mix is dosed with a flocculant prior to separation in a clarifier. The settled sludge is either recycled to the lime/sludge mix tank (retention time is greater than 1 second), or removed from the system as waste sludge. The clarified water is discharged to the environment. The amount of sludge recycled is controlled by the sludge recycle ratio used, that is the ratio of solids recycled to the new solids precipitated from the minewater, and is typically between 20 and 30 kg of recycled solids per kg of new solids precipitated from the minewater.

It was claimed that the process produced a sludge that settled to between 15% and 50% w/w, depending on the ratio of Fe (II) to Fe (III) in the feed water. At a high Fe (II) content, the sludge settled to approximately 50% w/w, whilst if the iron was in the form of Fe (III), the sludge can settle to above 15% w/w, with reported ratios and settled sludge concentrations presented in Section 2.8.1.

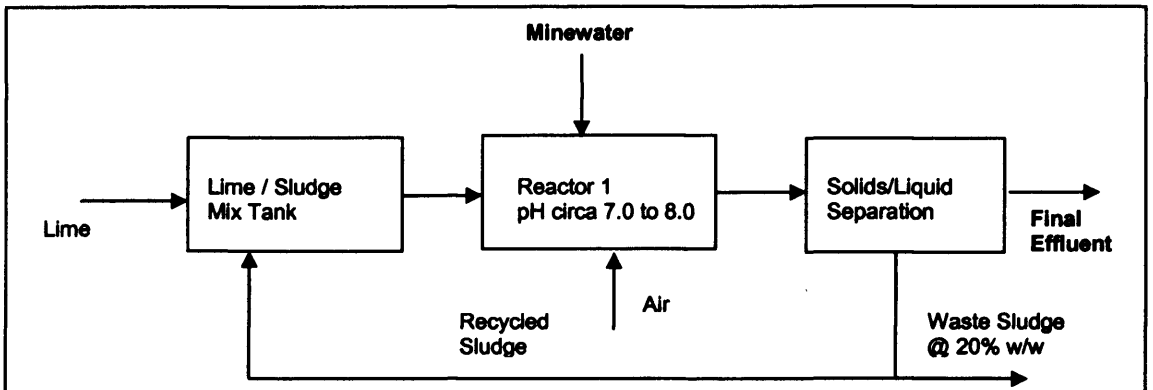


Figure 2.9: The BSC Type I HDS Process (Kostenbader, 1971)

Kostenbader *et al.* (1970) were unclear as to how the dense sludge was formed, but outlined the key operating parameters that lead to the formation of HDS. These were:

- Fe (II) to Fe (III) iron ratios in the feed water;
- Ratio of solids recirculated to new solids precipitated;
- Point of alkalinity addition;
- Neutralisation pH; and
- Retention time.

Depending on the feed water used, HDS was formed in between 5 days and 10 days.

2.8.1 Fe (II) to Fe (III) Iron Ratios

Kostenbader et al, (1970), claimed that the ratio of Fe (II) to Fe (III) had an impact on the settled solids concentration. The results of the work undertaken are summarised in Table 2.9 and appear to show that, as the ratio of Fe (II) to Fe (III) iron increased, the maximum underflow solids concentration increased.

Table 2.9: Reported effect of Fe (II) to Fe (III) ion ratio on settled solids concentration (Kostenbader et al, 1970)

Water Source	Fe (II) iron, Average % of total iron	Maximum concentration of settled solids (% w/w)
Minewater 1 (Fresh)	90	40
Synthetic minewater	>95	50
Synthetic steel pant water	>95	45
Steel plant water	>95	45
Minewater 1 (Old)	70	22
Minewater 2	30	15
Minewater 3 (Old)	2	18

2.8.2 Ratio of Solids Recirculated to New Solids Precipitated

The key parameter controlling the sludge density was reported as the ratio of solids recirculated to new solids precipitated. By controlling the recirculation ratio, an optimum settled solids concentration was calculated without affecting the clarifier surface area requirements. By operating the HDS plant with a recirculation ratio of between 25 and 30: 1, the maximum settled sludge densities were achieved. This resulted in a minimum (about 20%) increase in the clarifier surface area requirement compared to that for conventional lime neutralisation plant.

2.8.3 Point of Alkali reagent Addition

Altering the point of alkali reagent addition was trialled during the BSC test work. This involved trialling different configurations including, mixing the minewater and recirculated sludge with the alkali reagent in only one reactor, running as a Type I HDS plant and running as a Type II HDS plant. When all inputs were mixed in one reactor a gelatinous sludge was formed, whilst running in Type II HDS compared to Type I HDS resulted in a 50% decrease in maximum settled solids concentration.

2.8.4 Operating pH

Operating with a reactor pH of between 7.2 and 7.7 allowed for full oxidation of Fe (II) to Fe (III) iron and produced the maximum settled sludge density. Operating at a reactor pH of between 6.0 and 6.5 did not allow enough time for full oxidation of the Fe (II) to Fe (III) iron in the reactors used. Operating at a pH of 8.5 increased the clarity of the discharge water, though reduced the maximum settled sludge

density from 35% to 20% w/w solids and resulted in a requirement to increase the clarifier area by a factor of 1.6. Whilst running at a pH of between 9.0 and 9.5, a "rubbery" sludge was produced with an apparent high viscosity, as the sludge was difficult to pump.

2.8.5 Retention Time

The lime and recirculation sludge mix was estimated to be instantaneous, however the lime/sludge mix tank was sized at 1 minute. Reactor 1 was sized to provide a 10minute retention time, though this depended on the operating pH and Fe (II) concentrations in the minewater. Enough oxidation time has to be provided for in Reactor 1.

2.8.6 Additional Observations

When the plant was run at high flow rates, the discharge contained high concentrations of fine solids, and the use of flocculants was found to be ineffective in assisting with removing the fine solids.

The alkali reagents used were calcium carbonate, hydrated lime (calcium hydroxide), sodium hydroxide, dolomitic lime (calcium magnesium carbonate) and magnesia.

The alkali reagent efficiency was noted to increase when a pre-aeration stage was installed, reducing the lime demand by as much as 25%, due to stripping CO_2 from the minewater.

The sludge was more stable than conventional lime neutralised minewater, resulting in the ability to dispose of the sludge underground. Even when the sludge came into contact with acidic minewater, the metals were not resolubilised. Sludge dewatering trials were successful with both a filter press and a centrifuge.

2.8.7 Further HDS Developments by BSC

On the 21st March 1973 (Herman *et al.*, 1973), BSC filed an application for using an improved HDS process for removing cyanide and colour from coke plant wastewater. This application was granted on 12th November 1974.

BSC reported further improvements in the HDS process in 1983 (Herman *et al.*,

1983), when they reported a 40% reduction in lime use due to installation of a pre aeration tank. The HDS plant was reported to help with scale (calcium carbonate) build up. Discharge limits for iron, manganese and solids where achieved without the use of a flocculant. The manganese was removed at a pH of 9 with the HDS plant, compared to an operating pH of 10.0 in a conventional lime neutralisation plant. Comparable reductions in sludge volumes between the HDS plant and a conventional precipitation plant, as found by Kostenbader *et al.* (1970), were reported.

BSC applied for a European patent in 1983 (Herman *et al.*, 1983) for using a carrier material (silica, sand, oxides of heavy metals) to be mixed with the neutralising reagent in Reactor 1 (lime/sludge mix tank), instead of recycled sludge. The neutralising reagent was thought to adsorb to the surface of the carrier and then passed to the reactor for treatment of acid minewater (or industrial waste waters). The heavy metals in the minewater would then precipitate out and a flocculant was added to the mix prior to settlement in a clarifier. If required, the settled sludge could be recycled as described in Section 2.8.1. This treatment process reportedly improved the treated water quality and was able to remove most heavy metals, including manganese and cadmium, without having an effect on the settled solids concentration.

2.8.8 Tetra Technologies and the HDS Process

Tetra Technologies acquired the legal rights to the BSC HDS process in 1990. During the early part of the 1990s, Tetra Technologies further refined the Type I HDS process by suggesting the installation of a classification/bypass stage between Reactor 1 (now termed as the Precipitation Reactor) and the solids/ liquid separation stage, as shown in Figure 2.10. The primary function of this new stage was to reduce the solids loading on the solids/liquid separation stage when wastewaters (and minewater) of high contaminant concentrations were to be treated. However, the classifier also separates according to size of particles, allowing large particles to be removed from the system and small, finer particles to be retained in the system. Patents were awarded in the US (Wentzler *et al.*, 1990a) and Internationally (Wentzler *et al.*, 1990b) in 1991, and in Europe in 1994 (Wentzler *et al.*, 199c).

When wastewaters with high contaminant concentrations are treated, high

concentrations of new solids are precipitated. Linking this with the requirement for a solids recycle ratio of approximately 25: 1 (Kostenbader *et al.*, 1970) there is likely to be a very high solids loading on to the clarifier (solids/ liquid separation unit). As the surface area of a clarifier is sized according to the settlement velocity and solids loading on to the clarifier (Coe *et al.*, 1916), this can result in a clarifier with a large surface area. By installing a classifier (e.g. hydrocyclone) or simple sludge bypass line, with solids being returned to the lime/ slurry mix tank (now termed as an Adsorption Reactor, Figure 2.10)), the size of the clarifier could be reduced due to the reduced solids loading.

Additionally, it was suggested that by using a classifier, the large particles (that may not compact as well) in the underflow should be removed from the system.

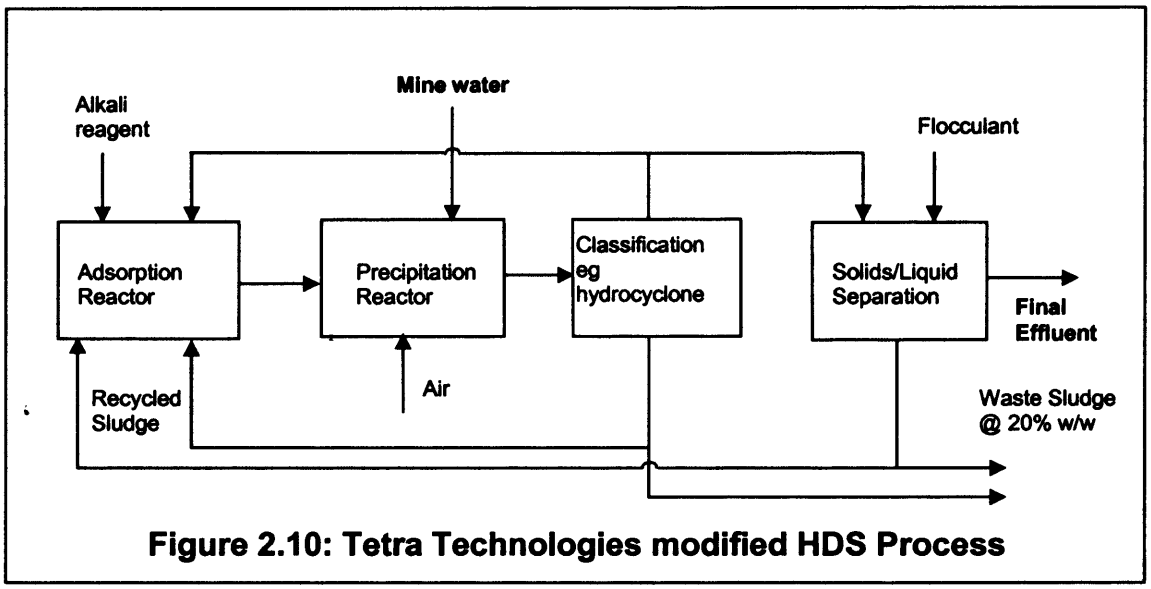


Figure 2.10: Tetra Technologies modified HDS Process

Wentzler *et al.*, 1990, further developed the theory that the neutralising reagent was adsorbing (Herman *et al.*, 1983) to the surface of the recycled sludge, due to surface effects and the dissolved metals were precipitated out in Reactor 1 (Precipitation reactor). However, the description of the mechanisms involved was unclear and no testing of the mechanisms appeared to of been undertaken. However, it was considered that particle size, surface effects, adsorptive forces and ionic reactions were key to the formation of HDS. It was understood that by mixing the recycled sludge with the alkaline reagent, the recycled particles appeared to act as nucleation sites for the hydroxides in the Adsorption Reactor. These sites then attract more hydroxides, which in turn attract the dissolved metals. This was thought to lead to layers of new metal hydroxides to be generated on the surface of the recycled sludge. This continued until the particles became large enough to be removed from the system by the clarification stage.

2.8.9 Work Undertaken in South Africa

During the 1970's, work was undertaken at Coronation Collieries, Kromdraai, South Africa using a Type 1 HDS system for treating the minewater from the disused mine by Anglo American Research Laboratories (Bosman, 1974). After initially considering conventional chemical precipitation, using calcium hydroxide, the use of a Type 1 HDS system was reviewed due to problems experienced with the volume and mass of sludge being generated. Tests using the Bethlehem Steel Corporation HDS process were successful with an underflow solids concentration of 22% w/w being obtained. Bosman (1974) found that critical to the formation of high underflow sludge densities was:

- A minimum mixing time of 20 minutes for the lime slurry and the recycled sludge in the lime/sludge mix tank (Figure 2.8),
- The degree of agitation in the lime/sludge mix tank (mixer impellor blades should not rotate faster than 4 m/s),
- A minimum retention time of 5 minutes was required in Reactor 1,
- The required sludge recirculation ratio was in excess of 20 to 1.

Problems with discharge solids concentrations were experienced, with suspended solids concentrations as high as 60 mg/l being detected, even with a relatively low clarifier rise rate of 0.57 m/hour. Flocculant was added to the clarifier feed to assist with the removal of the suspended solids in the discharge water, however this was not successful and lowered the underflow sludge density. The clarifier underflow was also reduced from 22% to 12% w/w, when calcium carbonate was used as the alkali reagent instead of calcium hydroxide.

As an explanation of how HDS was formed, Bosman (1974) suggested that sludge particles generated during conventional precipitation form a water layer around the sludge particles due to the hydrous nature of the iron. The absorption of hydroxyl ions, hydrogen and/or metal cations formed electrical double layers around the sludge particles which contain potential determining ions and counter ions. The electrostatic (zeta) potential caused the sludge particles to repel each other and hence form a voluminous sludge. By reducing the volume of water adsorbed, or by altering the repelling force, a denser sludge could be produced. Therefore, Bosman (1974) suggested by controlling the rate of precipitation a denser sludge could be formed. Mixing the lime slurry with the recycled sludge before contacting

the minewater resulted in reducing the lime slurry pH from 12 to 10, resulting in slowing the rate of precipitation, and hence forming a denser sludge. Additionally, calcium ions lower the electro kinetic potential and would eventually reduce the size of the double layer (also see Section 7.4.2), however no zeta potential measurements were taken to confirm this. Due to Fe (III) precipitating at a lower pH than Fe (II), as the low pH of the minewater is raised the Fe (III) is precipitated leaving the unoxidised Fe (II) in solution. The Fe (II) is then adsorbed as counter ions, which again compresses the double layer and reduces the zeta potential. Finally, Bosman (1974) suggested that aging densifies the sludge by dehydration and then the formation of Fe-O-Fe linkages.

During the early 1980's, Anglo American Research Laboratories undertook further studies on the HDS process and cited the following as key in the formation of sludge with high densities (Bosman, 1983):

- Ratio of solids recirculated to solids precipitated from solution.
- Retention time in lime/sludge mix tank.
- Peripheral velocity of lime/sludge mix tank mixer impellor.
- Total iron content of the acid minewater.
- Oxidation state of the acid minewater, i.e. ratio of Fe (II) to Fe (III).
- Amount of calcium sulphate precipitated from solution.

These parameters are very similar to the parameters suggested by Kostenbader *et al.*, 1970, which is unsurprising as the work undertaken by Bosman (1983) mirrored the work undertaken by Kostenbader.

As with Kostenbader (1970), Bosman (1983) used a similar layout of reactors and tanks, however Bosman used different terminology for the process involved. Figure 2.11 shows that Bosman considered that sludge 'conditioning' was taking place in the lime/sludge mix tank (as defined by Kostenbader in Figure 2.9), whilst minewater neutralisation continued to occur in the Reactor tank (as defined by Kostenbader in Figure 2.9).

Time restrictions imposed on Bosman (1983) meant little work was done on how HDS is formed, however the process was trialled on a number of sites with general success. The results of the trials are summarised in Table 2.10.

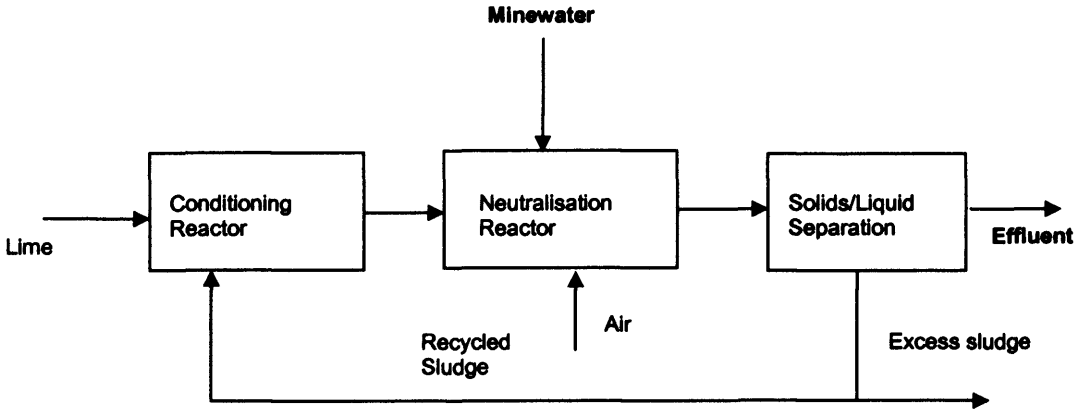


Figure 2.11: Bosman (1983) flow diagram of the HDS process

Table 2.10: Densities of sludges formed by conventional precipitation and by the HDS process (Bosman, 1983)

Case no	Unit	1	2	3	4	5
Feed water						
Total iron	mg/l	780	250	880	4600	50
Total dissolved solids	mg/l	7700	1800	7600	22500	2100
Conventional Process						
Precipitated solids (pH 7.5 and 1 hour settlement)	mg/l	1600	900	2400	31000	135
Sludge volume	ml/l	80	90	500	400	13
Sludge density	g/l	20	10	5	80	10
HDS process						
Sludge volume	ml/l	8	4	20	80	1
Sludge density	g/l	210	220	120	390	150

During the tests, subtly different minewater characteristics were trialled from use of pre treatment liming (Case 1), varying Fe (II) to Fe (III) ratios (Case 2), high Fe (III) to Fe (II) ratio (Case 3), batch testing with high Fe (II) concentrations (Case 4) and low iron and acidity concentrations (Case 5). Case 3, which had high Fe (III) to Fe (II) ratios, indicated lower sludge densities, whilst the very high Fe (II) concentrations during Case 4 produced the high sludge densities during the laboratory batch tests.

The Bosman (1983) laboratory batch test methodology was used to 'screen' minewater for the suitability with the HDS process. This has been further modified and used for laboratory batch tests undertaken during this research (Chapter 5).

Bosman undertook further work on the impact that the HDS process had on calcium sulphate precipitation. The scale build up was reduced by use of the HDS process, with Bosman hypothesising that the recirculated sludge acted as seeding the process with calcium sulphate crystals. This added to the benefits of the HDS process.

2.9 Alternative Type I High Density Sludge Processes

2.9.1 Noranda HDS Process

The Noranda HDS process is based around a Type I HDS system, with the US patent application filed on 22nd October 1993 (Kuyucak *et al.*, 1993) and awarded 27th June 1995. In the Noranda process, minewater is mixed with a proportion of the recycled settled solids to raise the pH in Reactor 1 to between 4.0 and 4.5 (a schematic of process is shown in Figure 2.12). If required, lime is used to assist this process. The operating pH of Reactor 1 ensures that only iron present as Fe (III) is precipitated (as Fe (III) hydroxide) in Reactor 1 with all other metals remaining in solution, whilst other metals returned in the recycled sludge are dissolved. Calcium sulphate may also be removed in Reactor 1. The precipitates formed in Reactor 1 form stable crystals that act as nuclei in Reactor 2 where crystallisation is promoted.

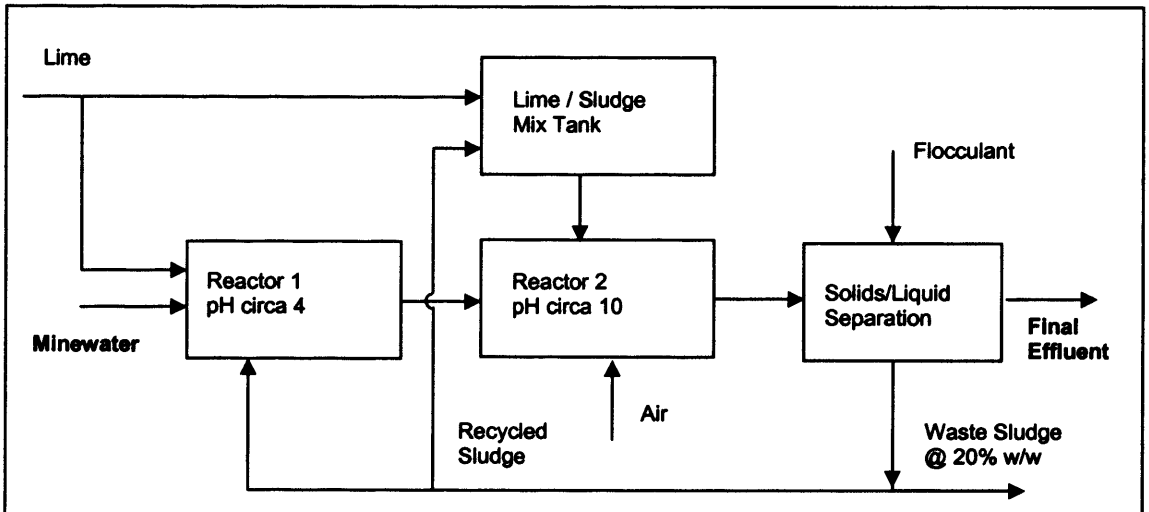


Figure 2.12: Noranda HDS process (Kuyucak *et al.*, 1993)

The pH is then raised to between 9.0 and 10.0, depending on the metals to be removed in Reactor 2, by using a lime/sludge mix. Air is also introduced to ensure all Fe (II) is oxidised to Fe (III). This stage removes all other metals from solution. The resultant sludge/ liquid mix is dosed with flocculant prior to discharge of

clarified water. The settled sludge is either recycled to Reactor 1, to the lime/sludge mix tank (approximately 1/5 of that recycled to Reactor 1), or removed from the system as waste sludge.

It is claimed that this process produces a denser, more stable sludge by doing the following:

- Iron present is removed as Fe (III) hydroxide in Reactor 1, forming crystals that act as nuclei for the metals removed in Reactor 2. Calcium sulphate crystals are also produced in Reactor 1. Due to the operating pH, other metals (e.g. zinc) are left in solution and do not affect this process.
- The aeration process in Reactor 2 oxidises the Fe (II) to Fe (III), producing a more stable sludge.
- The process produces a granular sludge and uses less lime (10 to 20% reduction) compared with other HDS processes. The sludge is claimed to be more stable and approximately ½ the volume of sludge produced by other HDS process. However there is no evidence to suggest the Noranda treatment plants produce sludge of twice the concentration as a result of halving the sludge volume. The process is also claimed to reduce scaling (due to calcium sulphate) on pipe work.

2.9.2 Other Type I HDS Process Plants

In 1989, a Noranda type HDS plant was installed at La Mine Doyon, Quebec, Canada (Poirer *et al.*, 1997) designed by Tetra Technologies Inc. The sludge removed from the HDS plant for long-term storage averaged 20% w/w solids with a composition of 52% gypsum, 24% Fe (III) hydroxide, 12% aluminium hydroxide and 6% magnesium hydroxide. Compliance with the conventional solid waste leachate test and the modified leachate tests was shown. However, no further explanation for how the process worked was given.

Vachon *et al.* (1987) reported in depth the use of lime in the active treatment of minewater and options for disposing of sludge generated in active treatment. Various means of densifying the sludge including the HDS process were looked at. The advantages and disadvantages of using the HDS process compared to conventional lime precipitation were reported and are presented in Table 2.11.

Table 2.11: Advantages and disadvantages of the HDS process over conventional precipitation, (Vachon *et al.*, 1987)

Advantages	Disadvantages
Minimal land use. Reduced volume of sludge for disposal. May be suitable for long-term storage.	Higher capital, operating and maintenance costs. Operation requires closer control

Vachon *et al.* (1987) also reported on the means of thickening sludge generated during active treatment of minewater, including sludge pond design optimisation and mechanical dewatering. The work also looked at long-term disposal methods of the sludge generated. However, no explanation of hypothesis on how the HDS process works was given.

Type I HDS plants are used across Canada and worldwide. The experiences gained at several of the plants have been reported in the literature including the following plants:

- Cominco'c operations at Kimberley British Columbia Canada (Kuit, 1980), which was commissioned in 1979,
- Mattabi Mines Ltd HDS plant which also uses Tiltable Plate Settler (lamella clarifier) (Gauthier, 1980).
- Hudson Bay Mining and Smelting Co Ltd, constructed in 1974 a HDS plant treating a zinc waste, containing between 30 and 60 mg/l, producing sludge at an average of 13.5% w/w and a maximum of 19.0% w/w (Typliski *et al.* 1980). Experience gained in the Pennsylvanian Coal Mines (i.e. Kostenbader *et al.*, 1970) helped develop the understanding that made the construction of this plant possible.
- Brunswick Mining and Smelting HDS Plant at Bathhurst, N.B., Canada which, was commissioned in 1993 (Murdock *et al.*, 1994).
- Type I HDS plants are also reported to be in use at Tiwest, Kwinana, W.A., Australia (Murdock *et al.*, 1994), Glenbrook Nickel Co., Coos Bay, OR, U.S.A. (Murdock *et al.*, 1994) and Cajamarquilla Refinery in Chile (Fernandez *et al.*, 2000).

However, little or no explanation was reported in the papers above as to how the

HDS process actually works.

2.10 The Type II HDS Process

In the Type II HDS process, recycled sludge is mixed with the minewater in a first stage reactor (Reactor 1 or Stage I reactor), Figure 2.13. This raises the pH of the minewater to between 7.0 and 8.0, depending on minewater chemistry and recirculation rates, resulting in the removal of a high proportion of the metals from solution (Aubé *et al.*, 1997; and Chapter 4). The pH in the Stage I reactor is not controlled but varies with recirculation flow rates, which, as with Type I HDS, are controlled at approximately 25 kg of recirculated solids to each kg of new solids precipitated from the minewater. The minewater sludge slurry is dosed with lime (or alternative alkali reagent) in the second stage reactor (Reactor 2 or Stage II reactor). Air is also introduced to oxidize Fe (II) to Fe (III) in the Stage II reactor. The fully oxidised slurry is dosed with flocculant and then flows to a clarifier for solids/ liquid separation. The clarified water is discharged to the environment whilst approximately 95% of the settled sludge is recirculated to the Stage I reactor, with the remaining 5% of settled sludge "wasted" from the system.

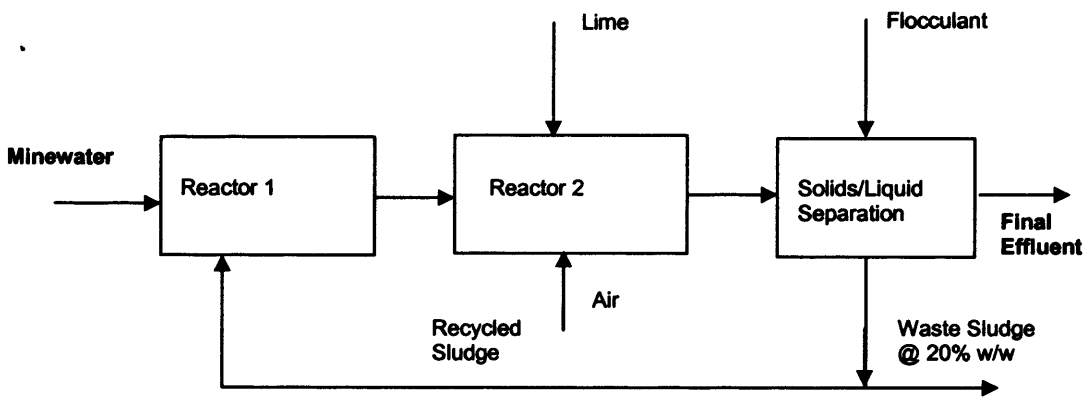


Figure 2.13: The Type II HDS process (Keefer *et al.*, 1983; Coulton *et al.*, 2003b; Aubé *et al.*, 1997, Kuyuack *et al.*, 2001)

Kostenbader *et al.* (1970) reported trialling the Type II HDS process with little success. Keefer *et al.* (1983) had success generating Type II HDS when HDS sludge was formed during batch treatment trials, researching the conversion of minewater treatment sludge into a coagulant. These trials indicated that a lime saving of in excess of 31% was achieved, in comparison to conventional chemical precipitation.

During the 1990's, Noranda Technology Centre and Unipure Environmental independently developed Type II HDS. Unipure Environmental modified their patented wastewater treatment method (Walker, 1989) by recirculating sludge to a "Pre- reactor", whilst Noranda developed a Type II HDS process to treat the minewater from the Geco mine (Aubé *et al.*, 1997).

Typical examples of the Type II HDS process can be found at Wheal Jane in Cornwall, UK (Coulton *et al.*, 2003b;); Horden, County Durham, UK (Coulton *et al.*, 2004) and Geco Mine, Ontario, Canada (Aubé *et al.*, 1997).

During early pilot plant work at the Geco mine, the sludge was not pumpable due to the sludge having a high viscosity, which was attributed to low initial sludge recycle ratios. However, once the sludge recycle ratios were increased, the viscosity dropped and the sludge became pumpable, resulting in recycled sludge concentrations of approximately 35% w/v. Sludge microscopic analysis (SEM) indicated that the sludge generated became more compact and the particles became more spherical in form when higher sludge recycle ratios were operated. This could be explained by 'Einstein's equation of viscosity of dispersions', presented in Equation 2.8 (described by Hiemenz *et al.*, 1997), where Einstein showed that stiff rods gave a much more viscous solution than spherical particles. Therefore, as the sludge generated at Geco mine became more spherical, the viscosity would have reduced.

Einstein's equation of viscosity of dispersions:

$$\mu = \mu_0 (1 + k \Phi) \qquad \text{(Equation 2.8)}$$

Where:

μ is the viscosity of the liquid (Pa s)

μ_0 is the viscosity of medium (Pa s)

k is the constant according to shape of particle (2.5 for spheres)

Φ is the volume fraction of the particles

Aubé *et al.* (1997) suggested that as a consequence of the increased recycle rates, the Reactor 1 pH was increased to a level that resulted in the precipitation of most of the heavy metals, 99% of Fe, Zn and Al were measured to have been removed from solution. It was hypothesised that the recycled sludge was acting as

a seeding point for the metals precipitated in Reactor 1. Aubé *et al.* (1997) concluded that critical to the formation of HDS sludge was controlling the system pH, which was attributed to the system carbonate chemistry.

The required retention times in the reactors were investigated with recycle sludge of 12% w/w dried solids being generated when the Reactor 1 retention time was reduced from 30 min to 5 min. The retention time in the whole system was considered important in the gypsum formation. The retention time in the pilot plant was less than that in the full-scale plant operation at the time, resulting in limited gypsum being formed. At Geco, due to the increased stability of the sludge formed, the waste minewater sludge was disposed of underground in old mine workings.

The Type II HDS plant operated at Wheal Jane, Cornwall, England (as described in Chapter 4 and by Coulton *et al.*, 2003b) has also produced a similar plant performance to that reported for a Type I HDS plant. Horden MWTP, where the minewater contains high levels of salinity (Coulton *et al.*, 2004a), in the North East of England also uses a Type II HDS treatment plant in order to reduce the volume of sludge produced.

2.11 HDS Sludge Process Developments

In recent years, work has been undertaken on understanding how the HDS process produces sludge of high solids concentration (Zinck *et al.*, 2001; Dempsey *et al.*, 2003), which has led to further developments of the HDS treatment process. This work has concentrated on nucleation and crystal formation (Stumm *et al.*, 1996), with nucleation (i.e. precipitation of metals) able to take place on a solid surface (heterogeneous) or in a solution (homogeneous). Controlling the level of supersaturation will control the location of nucleation. At low supersaturation levels, heterogeneous nucleation occurs and at high supersaturation levels, homogeneous nucleation occurs (Stumm *et al.*, 1996; Dempsey, 1993, Schwertmann *et al.*, 2000). A more detailed explanation of nucleation and crystal growth is given in Chapter 8 and is available in the literature (e.g. Stumm *et al.*, 1996, Schwertmann *et al.*, 2000).

A multi stage-neutralisation process (Demopoulos *et al.*, 1995) has been developed (with a US patent awarded in 1997 (Demopoulos et at., 1995)), which employs controlled neutralization in a series of reaction tanks operating at different

pH values. That is, the acid minewater is neutralised in a series of reactors by the addition of the alkali reagent and the recirculation of settled sludge from the base of a clarifier (as in Type II HDS). By controlling the pH in each of the reaction tanks, the supersaturation levels are controlled, which reportedly encourages crystallization. It was reported that a solids concentration of 55% w/w was achieved using NaOH as the alkali reagent, and 67% w/w using lime as the alkali reagent (Demopoulos *et al.*, 1995) when treating a synthetic minewater with the initial concentrations of 1000 mg/l of Fe^{3+} and 6000 mg/l of SO_4. However, due to the high SO_4 concentrations, 66.5% of the solids were gypsum, though this was in a distinct phase to that of the FeOOH, which was 33.5% of the solids. No plants have been constructed as of yet.

Dempsey (1993) investigated how the control of nucleation/crystal growth rates affected the production of HDS sludges. Bench scale tests were undertaken on synthetic solutions with different processes and mechanisms tested to see the impact on the sludge formed. These were:

- The Type I HDS process,
- Manipulation of the zeta potential during the precipitation of Fe (III) hydroxide,
- Minimising supersaturation rates to limit the rate of primary particle (new) formation,
- Precipitation of Magnetite by manipulation of Redox and chemical composition,
- Physical/chemical disruptions to convert low density sludge into HDS sludge.

Dempsey (1993) suggested that by controlling the degree of supersaturation, the new amorphous phases do not form new primary particles, but allow crystal growth or heteronucleation to occur, resulting in high density sludge formation, and whenever supersaturation did happen, homonucleation occurred rather than crystal growth. The process can be controlled by controlling the recirculation rates, as crystal growth is proportional to the solid's surface area. Magnetite precipitates were formed by controlling the oxidation rates at pH circa 9. This was achieved by the slow diffusion of oxygen (or hydrogen peroxide) into the settled sludge, this sludge resulted in a settled sludge with a decreased volume. Fractal aggregates were formed whenever conditions allowed the immediate precipitation of Fe (III)

hydroxide, which were inert to physical and chemical disruptions. By controlling the pH and zeta potential a four fold increase in the density of the sludge was produced.

Morgan *et al.* (2001 and 2003) reported a laboratory developed one-step low temperature ferrite process that was capable of producing magnetite sludge, compared to amorphous Fe (III) hydroxide sludge. This process used controlled aeration of the recycled sludge and/or the sludge/minewater oxidation reactor at a pH of circa 10.5 (a possible formation pathway is shown in Figure 2.6). This HDS process development would appear to be similar to that developed and reported by Dempsey (1993). The sludge generated was reported to have good stability, similar to those of HDS sludge, and that was easily dewatered. However, due to the formation of magnetite, a more stable sludge was reported due to the increased crystallisation. No plants have been constructed as of yet.

2.12 Comparison of Sludge Produced by Different HDS Treatment Systems

The use of the HDS sludge treatment process greatly affects the characteristics of the sludge generated that requires subsequent disposal. The sludge characteristics, including percent solids (Zinck, 1997; Kostenbader *et al.*, 1970; Bosman, 1983; Aubé *et al.*, 1999), the particle size (Zinck, 1997; Aubé *et al.*, 1999), the sludge composition (Zinck, 1997; Aubé *et al.*, 1999), the mineralogy and morphology (Zinck, 1997; Aubé *et al.*, 1999), the dewaterability of the sludge (Kuyucak, 2001; Zinck *et al.*, 2001) have been reviewed and the effect of the treatment process employed.

2.12.1 Percent Solids

Zinck (1997) reported solids concentrations from various minewater treatment plants ranging from 2.4% w/v (basic neutralisation) to 32.8% w/v (HDS system). Aubé *et al.* (1999) reported similar concentrations with 32.8% w/v at Brunswick Type I HDS plant and 27.8% w/v at the Geco Type II HDS plant.

Zinck *et al.* (2001) undertook pilot plant trials to compare the various forms of the HDS sludge process. During these trials, the Stage-neutralisation process produced sludge with an underflow concentration of 23.3% w/v, compared to 13.9% w/v for the Geco process and 11.0% w/v for the Tetra process. However,

the recirculation ratios of approximately 20:1 used during these trials was lower than the standard 25:1. Work undertaken during this research has shown that when high 'other' ions are present, such as chloride, calcium and magnesium (see Chapters 5 and 6) higher recirculation ratios are required. Hence, if the ratios had been increased this may have increased the sludge concentrations and decreased the sludge volumes produced.

2.12.2 Particle Size

Particle size distributions undertaken by Zinck *et al.* (2001) reported that the average particle size produced by the various HDS process was between 5.3 μm and 8.3 μm and that high density sludges tend to have lower median particle sizes compared to other treatment sludges (Aubé *et al.* 1999). Zinck also reported that an inverse trend existed between the sludge density and the median particle size, and that denser sludges displayed lower mean particle size distributions possibly due to better packing and less void space.

Aubé *et al.* (1999) reported that the sludge generated at the Geco mine (Type II HDS plant) had a median particle size of 2.89 μm, which was smaller than the sludge generated from other active treatment plants.

2.12.3 Sludge Composition

The composition of sludge generated during minewater treatment is affected by the treatment process, reagents used, but more importantly the minewater composition. The percentage of iron in the sludge removed from various active treatment plants varied from 2.3%, at the Kidd Metallurgical basic lime plant (Aubé *et al.*, 1999), to 46.5%, at the Geco Type II HDS plant (Aubé *et al.*, 1999). However, the chemical composition of the minewater, e.g. iron concentration as a percentage of the total metal concentration, and the presence of other elements, e.g. carbon dioxide, was not reported, hence it is difficult to compare one plant with another...

2.12.4 Mineralogy and Morphology

Common to the majority of treatment processes used for treating minewater, the HDS process leads to the formation of amorphous hydroxide sludges. These amorphous sludges were reported to assist with the removal of metals from the

minewater (Aubé *et al.*, 1999).

Zinck (1997) reported that most sludges generated in the active treatment of minewater are amorphous in form. However, Zinck (1997) also reported that the presence of calcite and gypsum in aged sludges gave a more crystalline structure to the sludge and increased the stability of the sludge. Zinck (1987) also reported a more stable sludge with the presence of carbonates and silicates.

Aubé *et al.* (1999) reported that the Geco mine generated sludge contained a crystalline iron compound, Lepidocrocite (γ-FeO(OH)), possibly due to the high concentration of Fe (II) in the minewater, see Figure 2.6 for schematic of iron oxide formation. (Lepidocrocite was also detected during the continuous pilot plant trials undertaken in the present research (Trial 1-Iron in Tap Water), Section 7.3.1.)

2.12.5 Sludge Stability

The sludge stability is reportedly increased when the sludge is produced during the treatment of minewater by the HDS treatment process, Section 2.13.4. The leachability of metals from sludge is pH dependent (Vachon *et al.*, 1987), with zinc the metal most commonly detected in the leachate released during leach testing (Aubé *et al.*, 1999; Zinck, 1997). Due to the final pH of the stage-neutralisation process being lower pH when compared to Type I and Type II HDS systems, metals tend to be released more readily from solids produced by this process (Zinck *et al.*, 2001).

2.12.6 Settlement Velocity

A fundamental function of the treatment of minewater is the need to separate the precipitated solids from the treated water. This treatment stage is commonly achieved by gravity separation in clarifier settlement tanks; other options are available such as dissolved air flotation (Bosman, 1983). Critical to the operation of clarifiers is the rate of sludge particle settlement and the volume of water that is discharged from the treatment plant. The settlement velocity is used to monitor the settleability of the sludge. During the trials, comparing the different HDS processes (Zinck *et al.*, 2001), comparable settlement rates were achieved for the Stage-neutralisation, Type I and Type II sludge settled at 23.7 m/hr, 17.3 m/hr and 21.9 m/hr respectively. However, this did not take into account the different solids concentrations, though the same flocculant dose was used during each of the

trials. The recorded settlement velocities at Wheal Jane MWTP of 18 m/hr (and presented in Chapter 4) are comparable to those measured by Zinck *et al.* (2001).

2.13 HDS Process Summary

Since the installation of the Bethlehem HDS treatment plant (Kostenbader *et al.*, 1970), numerous HDS treatment plants have been subsequently installed worldwide. The use of the HDS process improves the sludge settling and dewatering characteristics, and hence reduces the volume of the sludge to be disposed of.

The parameters suggested by Kostenbader (1970) (Section 2.8) and Bosman (1983) (Section 2.8.9) are still reported as key to the formation of HDS sludge.

Though the knowledge of the HDS process as a whole has increased greatly, the detailed scientific understanding of the mechanisms involved in the formation of HDS sludge have not been reported in the literature.

Work undertaken by Zinck and Dempsey in recent years has focused on the levels of supersaturation and hence nucleation and crystal growth. This would appear to be fundamental to the formation of HDS sludge.

The work undertaken in the present research, and reported in the subsequent chapters, has attempted to move the scientific understanding of the HDS process forward, and dispel some misconceptions and contradictory beliefs surrounding the HDS process.

3 WATER ANALYSIS TECHNIQUES

3.1 Introduction

Sludge and water samples were taken throughout the research and routinely analysed at Cardiff University (for samples generated during Chapters 5, 6 and 7), Wheal Jane Laboratories (for samples from Chapters 4, 5 and 6) and Swansea University (for Chapter 7). Various methodologies were used, depending on the location of analysis and the trials undertaken. Summarised below is a brief description of the methodologies used in each laboratory and a reference for a detailed description of the analytical procedure.

3.2 Analysis in Cardiff University

Analyses for Chapter 5 (Batch tests) and Chapter 6 (Continuous pilot plant trials) were undertaken at the Cardiff University Environmental Engineering Water Laboratories. Water and sludge samples were routinely analysed for total suspended solids concentration. Water samples were also analysed for total and dissolved metal and sulphate concentrations, whilst the dry solids were analysed for total metal concentrations.

3.2.1 Total Suspended Solids Methodology

The total suspended solids concentration was calculated by measuring the difference between the weight of a filter paper and the weight of a filter paper and dry solids after being dried at 105°C for a minimum of 2 hr. The full procedure and methodology is presented in "Standards Methods for the Examination of Water and Wastewater", Part 2540 C.

3.2.2 Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry Metal Analysis

Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry was undertaken by Jeff Rowlands of Cardiff University School of Engineering using a Perkin Elmer Plasma 400, with the machine controlled by an IBM compatible PC running dedicated software. A full description of the ICP operation and use can be found in "Standard Methods for the Examination of Water and Wastewater", Part 3120 B.

Prior to the analysis being undertaken the ICP was calibrated by Jeff Rowlands for each element to be detected, ensuring consistent accuracy. Standards were run at the start of each analysis. The analysis was undertaken by file method. The wavelengths and detection limit for each element are shown in Table 3.1.

Table 3.1: Wavelengths and detection limits of ICP analysis ("Standard Methods for Examination of Water and Wastewater")

Element	Wavelength nm	Estimated detection limit µg/l
Al	308.220	40
Ca	317.930	10
Cu	324.754	6
Fe	238.204	7
Ni	231.604	8
Mg	269.080	30
Mn	259.373	2
Zn	213.856	2

Samples were collected and analysed in batches of 10. If the length of time between the taking of the samples and the undertaking of the analysis was expected to be greater than 2 days the water samples were acidified with nitric acid. For dissolved metal analysis the samples were filtered using the procedure for measuring the total suspended solids (see Section 3.2.1) with the filtrate being captured and acidified with nitric acid.

Where the composition of the dry solids was to be measured, digestion of the solids was first undertaken prior to the use of the ICP. Digestion was carried out by Microwave-Assisted Digestion using nitric acid and hydrofluoric acid. A full description of the procedure used can be found in "Standards Methods for the Examination of Water and Wastewater", Part 3030 I and 3030 K.

3.2.3 Sulphate

Sulphate analysis was undertaken using a Hach Colorimeter (Hach, 1999), Method 8051. This method is an adapted form of the methodology presented in "Standards Methods for the Examination of Water and Wastewater". Suitable dilutions with distilled water were used, as the detection range was 0 to 70 mg/l.

3.3 Wheal Jane Limited Laboratories

The Wheal Jane Limited Laboratory is a commercial laboratory located on the site of the old Wheal Jane mine. The laboratory has ISO9001 accreditation of its paperwork system, and methodologies complying with standard procedures, however due to commercial confidentiality only procedure outlines are presented. The laboratory has developed a wealth of experience in analysing minewater and minerals. Analysis was undertaken at the Wheal Jane Laboratories for Chapter 4 and when additional analysis was required for Chapters 5 and 6.

3.3.1 Total Suspended Solids

Wheal Jane Laboratories undertake Total Suspended Solids analysis using the same methodology as described in Section 3.2.1.

3.3.2 Atomic Absorption (AA) Spectrometry Metal Analysis

Atomic Absorption (AA) Spectrometry was undertaken using a Thermo Electron SolAAr S4, with the machine controlled by an IBM compatible PC running dedicated software. A full description of the AA operation and use can be found in "Standards Methods for the Examination of Water and Wastewater", Part 3111 A.

Prior to the analysis being undertaken, the AA was calibrated for each element to be detected, ensuring consistent accuracy. Standards were run at the start of each analysis. All metals were analysed by standard reference AAS techniques with arsenic and aluminium analysed by nitrous oxide-acetylene flame method, and all other metals were analysed by air-acetylene flame method.

Samples were collected and analysed immediately they arrived in the laboratory. For dissolved metal analysis, the samples were filtered using the procedure for measuring the total suspended solids (see Section 3.2.1) with the filtrate being captured and acidified with nitric acid. Digestion of the dry solids samples, that were analysed for metal composition, was undertaken by hydrochloric acid digestion. A full description of the procedure used can be found in "Standards Methods for the Examination of Water and Wastewater", Part 3030 F.

3.3.3 Sulphate Analysis

Sulphate was measured by precipitation as a barium chloride precipitate. A full

description of the procedure used can be found in "Standards Methods for the Examination of Water and Wastewater", Part 4500 SO_4^{2-} C, Gravimetric method with ignition of residue.

3.3.4 Chloride

Chloride was analysed using a Xion 500 colorimeter using standard Chloride method LCJK311.

3.3.5 Carbonate and Hydroxide (Chemically Bound Water)

Carbonate and hydroxide (measured as chemically bound water) determination of the sludge samples was undertaken by measuring the dried solids content of a sample. The dried solids were then heated to 600°C for 1 hour, removed from the oven, cooled, and the weight of the dried solids measured. The solids were then heated to 1000°C for 1 hour, removed from the oven, cooled and the weight of the dried solids measured. The hydroxide (measured as chemically bound water) evolves between 200°C and 600°C and the carbonate evolves at between 600°C and 1000°C. This procedure is based on the ThermoGravimetry Analysis (TGA) procedure (Mendham *et al.*, 2000).

3.4 Sludge Characterisation Analysis

Sludge characteristic analysis was undertaken by performing X-Ray Diffraction (XRD) analysis, microelectrophoresis analysis and Scanning Electron Microscopy (SEM).

3.4.1 X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis of dried samples were conducted using topfill powder mounts and CuKα radiation on a vertical, wide range goniometer (Philips PW 1820-00) equipped with a 1° divergence slit, a 0.2 mm receiving slit, and a diffracted-beam monochromator. Specimens were scanned from 10° to 80° in 2θ increments of 0.02° with a 1-second step time. Peak positions were determined by using the Philips Xpert Industry software. Analysis of all samples was undertaken using an identical methodology. The analysis was undertaken by Jeff Rowlands, Cardiff University School of Engineering.

3.4.2 Microelectrophoresis Analysis

'Young' and 'old' sludge samples (see Chapter 7) generated during the continuous trials (see Chapter 6), were taken from continuous pilot plant trials 1 to 5 for electrophoretic mobility measurements. The measurements were undertaken by Paul Melvyn Williams at Swansea University using a Zetasizer 2000 (supplied by Malvern Instruments Ltd, Malvern, UK).

Electrophoretic mobility measurements of solids in pH corrected stock solutions

The dilute suspensions used for measurement of the electrophoretic mobility were made in the following manner:

1. 4 stock solutions of pH corrected de-ionised water were generated as presented in Table 3.2 for use with sludge generated during continuous trials 1 to 4. Dilute hydrochloric acid and sodium hydroxide were used to change the pH of the de-ionised water.
2. Approximately 2ml of the sludge was added to 40 ml of each of the pH altered de-ionised water.
3. The pH of the dilute suspension was taken.
4. The electrophoretic mobility was measured using the Zetasizer 2000.
5. For continuous trial 5 supernatant was decanted off the seawater sludge samples into measuring beaker.
6. Approximately 2 ml of the seawater sludge (Section 6.8) was added to 40 ml of seawater supernatant.
7. The pH of the dilute suspension was taken.
8. The electrophoretic mobility was measured using the Zetasizer 2000.

Table 3.2: Electrophoretic mobility measurements stock solutions

Solution	pH	Acid/alkali used
de-ionised water	3.8	Hydrochloric acid
de-ionised water	6.9	Hydrochloric acid
de-ionised water	8.9	Sodium hydroxide
de-ionised water	10.3	Sodium hydroxide
sea water 28/10/03	7.6	Supernatant water
sea water 29/10/03	7.7	Supernatant water

3.4.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was undertaken by Rolph Wheeler-Jones of the Cardiff University School of Engineering on samples of sludge taken during the research. From a bulk sample of sludge, a proportion of the material was collected in a pipette. The pipetted sample was then deposited onto an aluminium mounting stub, on which was a conducting carbon sticky tab. The sludge droplet was allowed to dry in air in a fume cupboard. The dried encrusted deposit was distributed with a fine sable hair brush, enabling fine material to be examined in due course. The deposited sample material was sputter coated with a conducting film. In this case, gold was used and deposited to a thickness of approximately 20Å. This thickness of material would not mask any of the detail on the particles being viewed with the SEM. The system used for sputtering was a 'Balzer Union' sputter coater now called 'Baltec'. Examination of the material was carried out with a JEOL scanning electron microscope model JSM6300. The batch test sample secondary electron images were recorded on film whilst the continuous trial secondary electron images were recorded on CD via a computer image capture system.

3.4.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) was undertaken by Professor Fred Pooley, with sample preparation by Mel Griffiths of the Cardiff University School of Engineering, on samples of sludge taken during the research.

From a bulk sample of dried sludge, a measure of the solids was removed and added to distilled water to produce a dilute suspension, which was sonicated for 10 minutes in an ultrasonic bath. Aliquots of the suspension were passed through a polycarbonated membrane filter (25mm 0.2μ pore size supplied, Nachpan Trak Etch Membranes). The samples were well dispersed over the filter paper, ensuring no aggregates or overlapping of solids. Several filter papers were prepared in case of aggregation. Strips of the filter papers were attached to a backing filter using cellotape and carbon coated in a carbon evaporating unit (Nano Tech (thin film) Limited, England). The filter papers were placed onto an electron microscope gold grid (150 mesh) and the filter paper removed in a chloroform bath. The prepared samples were then placed in the Technai 12 TEM for analysis. The images were taken and transferred to a PC for analysis using analySIS Imaging Processing

Software (commercial software supplied by Olympus Soft Imaging Solutions GmbH, Germany), with the processed images stored on CD. Chemical analysis of bulk and single particles was carried out by EDAX analysis (Energy Dispersive Analysis of X-rays). The TEM method is a modified standard procedure, which can be found in "Standards Methods for the Examination of Water and Wastewater", Part 2570.

3.4.5 Measurements of Sludge Filtration Characteristics

Piston press tests were undertaken on sludge samples taken at the end of each of the six continuous pilot plant trials (Chapter 7) and on a sample of 'single pass' conventionally precipitated sludge (Chapter 8).

Presented in Figure 3.1 is a schematic representation of the Svedala (Cornwall, UK) piston press, and photographs of each component can be seen in Figure 3.2.

The piston press was inverted and the piston placed inside the cylinder (diameter 0.076m, 1-litre in volume), with 'O' rings used to produce an air tight seal. 500ml of each sludge sample, at approximately equal sludge concentrations, was placed into the cylinder.

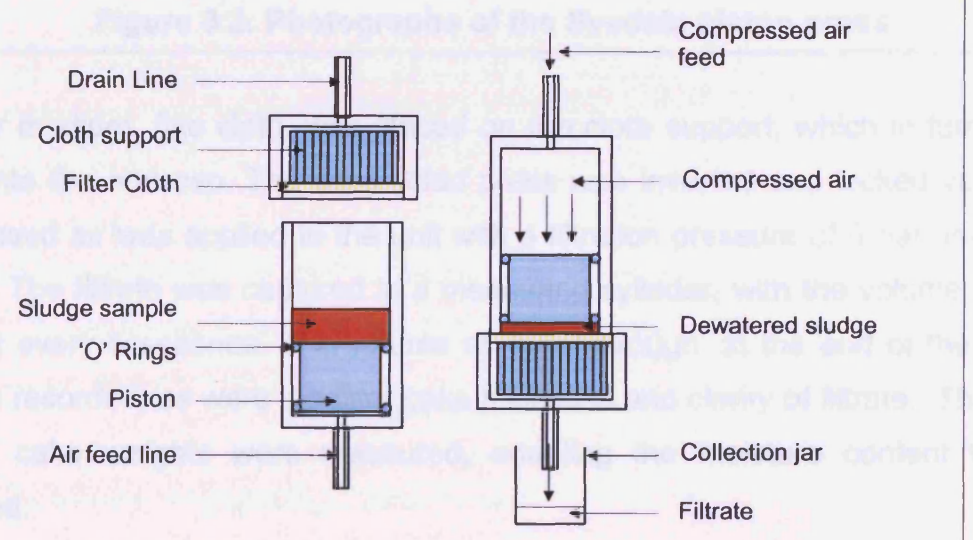


Figure 3.1a: Piston press components Figure 3.1b: Piston press in operation

Figure 3.1: Schematic diagram of the Svedala piston press

Figure 3.2a: Photograph of the piston press filter clothe support

Figure 3.2b: Photograph of the piston press end cap and piston

Figure 3.2c: Photograph piston press cylinder

Figure 3.2: Photographs of the Svedala piston press

The filter medium, fine cloth, was placed on the cloth support, which in turn was placed into the end cap. The assembled press was inverted and locked vertical. Compressed air was applied to the unit with a filtration pressure of 5 bar used for all tests. The filtrate was captured in a measuring cylinder, with the volume being recorded every 5 seconds. The volume at 'breakthrough' at the end of the tests was also recorded, as were the filter cake thickness and clarity of filtrate. The wet and dry cake weights were measured, enabling the moisture content to be calculated.

The data generated was analysed using the general filtration equation (Equation 3.1), valid for constant filtration area and pressure (Coulson *et al.*, 1991).

$$\frac{t}{V} = \frac{\alpha \mu c V}{2A^2\Delta P} + \frac{\mu R_m}{A\Delta P} \qquad \text{(Equation 3.1)}$$

Where:

t is the time in seconds (s)

V is the Volume of filtrate (m^3)

c is dry cake mass per unit Volume of Filtrate (kg/m^3)

α is the specific cake resistance (m/kg)

μ is the viscosity of the liquid (0.001) (Pa s)

ΔP is the pressure drop (Pa)

A is the filtration area (0.0045) (m^2)

R_m is the resistance of the filtrating medium (Cloth resistance) (m^{-1})

For a constant pressure with an incompressible cake, there is a linear relationship between t/V and V, and the slope of the line, a, and the interception, b, are defined by Equations 3.2 and 3.3.

$$a = \frac{\alpha \mu c}{2A^2\Delta P} \qquad \text{(Equation 3.2)}$$

$$b = \frac{\alpha \mu c R_m}{A^2\Delta P} \qquad \text{(Equation 3.3)}$$

By plotting the graph t/V against V, the slope of the line can be calculated, as can the point of interception, and hence the specific cake resistance and the cloth resistance can be calculated.

3.4.6 Centrifuge Dewatering Tests

Centrifuge tests were undertaken on 'young' and 'old' sludge samples (see Chapter 7) taken from the continuous pilot plant during the six trials using a Sigma 2-5 bench centrifuge (0-3900 rpm).

Thick walled Pyrex test tubes, of known weight, were filled with 10ml of sludge

samples of 'young' and 'old' taken during each of the trials. The sludge filled test tubes were weighed and then centrifuged at 500, 1000, 1500 and 2000 g for 5 minutes. Excess water was decanted from the wet centrifuge sludge and the weight of the test tubes containing wet solids recorded. The test tubes were then placed in an oven for 96 hours at 110°C for drying. After 96 hours of drying, the test tubes containing dried solids were weighed.

The initial (pre-centrifuge) solids concentration was calculated by use of Equation 3.4.

$$\text{Initial Solids (\% w/w)} = \frac{\text{((Test tube + dry solids) – (Test tube))}}{\text{((Test tube + water + solids) – (Test tube))}} \qquad \text{(Equation 3.4)}$$

The final (post-centrifuge) solids concentration was calculated by use of Equation 3.5.

$$\text{Final Solids (\% w/w)} = \frac{\text{((Test tube + dry solids) – (Test tube))}}{\text{((Test tube + wet solids) – (Test tube))}} \qquad \text{(Equation 3.5)}$$

3.4.7 Analytical errors

The major analytical errors associated with the present work have been calculated from the wide range of data available and are summarised as:

Suspended solids analysis ± 12.5%, depending on mass of sample with errors due to glassware, sampling and accuracy of balances.

Metal analysis of water ± 15%, with errors due to glassware and ICP instrument used.

Metal analysis of sludge samples ± 27.5%, with errors being a sum of errors in suspended solids analysis and in metal analysis of water.

Back calculation of material balances suggest that the carbonate and hydroxide concentrations reported are possibly underestimates by as much as 20%.

4 THE WHEAL JANE HDS MINEWATER TREATMENT PANT

4.1 Background

The outbreak of acidic minewater from the Wheal Jane mine site is the most infamous of its type in UK history, gaining worldwide publicity in 1992. This release of very low pH, highly metal laden minewater has been described in detail in the literature (NRA, 1994: Bowen *et al.*, 1998: Younger 2002). This chapter summaries the history of the Wheal Jane mine (including the outbreak in 1992), outlines the processes that were involved in the selection and construction (in 2000) of the Wheal Jane active minewater treatment plant (the first of it's type in the UK), and presents a review of the first 2 years operation (including the key operational parameters) and plant performance.

4.1.1 Wheal Jane Location

The Wheal Jane mine, and workings, are located in the catchment area of the River Carnon in the Carnon Valley, south west Cornwall, England (Figure 4.1). The Carnon River, which discharges to the Fal Estuary via Restronguet Creek and Carrick Roads, has a catchment area of 45 km^2 (Knight Piesold & Partners, 1999).

4.1.2 History of Mining in Cornwall

Mining commenced over two and a half thousand years ago in Roman times, and tin, copper, zinc and arsenic have all been mined. Tin was the primary metal mined during the 18th and 19th Century (Hamilton, 1963). Due to foreign competition, tin production declined from its heyday in the second half of the 19th century and, in 1997, the last remaining tin mine in Cornwall, South Crofty, closed.

The tin mining industry has been through a number of boom and bust periods and, as a result, miners from Cornwall, who were craftsmen in hard rock mining, have sought work all around the world during the 'low' periods. Thus giving the belief that at the bottom of every mine you will find a Cornishman.

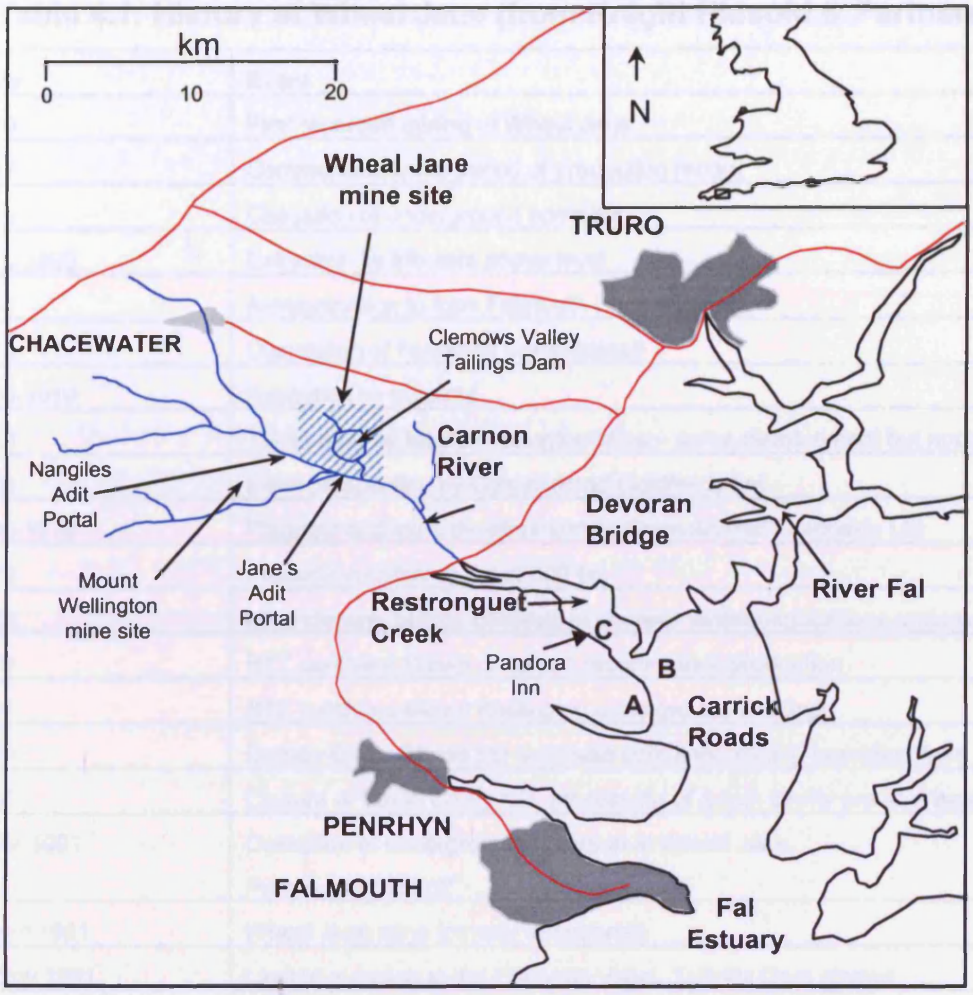


Figure 4.1: Location of the Wheal Jane mine (modified Younger *et al.*, 2005)

4.1.3 Mining in the Carnon Valley

The earliest record of mining in the Carnon Valley dates from around 2000 BC (Knight Piesold & Partners, 1995), and there is believed to have been continuous metal extraction from this catchment since that period. During the 17th Century, extensive mine development took place and by the early part of the 19th Century, the valley was a major world producer of tin (Hamilton, 1963). The western mining area of the Carnon Valley, Gwennap, was producing a third of the world's copper supply around the 1850's.

4.1.4 History of Wheal Jane Mine

A summary of key events in the history of mining and the treatment of acid minewater at Wheal Jane is presented in Table 4.1.

Table 4.1: History of Wheal Jane (from Knight Piesold & Partners 1995)

Date	Event
1740	First recorded mining at Wheal Jane
1847	Commencement of period of production record
1875	Cessation of underground operation
1875-1893	Extraction by tributers above level
1905	Amalgamation to form Falmouth Consolidated
1915	Dissolution of Falmouth Consolidated
1915-1919	Extraction by tributers
1939	Taken over by Mount Wellington Mine – some development but not completed
1966	Initial prospecting by Consolidated Goldfields Ltd
1966-1970	Planning and mine development by Consolidated Goldfields Ltd
1970	Production commenced at 600 t/d
1978	Mine closure, pumps continue to dewater whilst negotiations underway
1979	RTZ purchase Wheal Jane and recommence production
1981	RTZ purchase Mount Wellington underground workings
1985	Carnon Consolidated Ltd purchase combined mining operation from RTZ
1988	Closure of South Crofty mill, processing of South Crofty ore at Wheal Jane
6 Mar 1991	Cessation of underground operation at Wheal Jane. Pumps switched off
9 Sept 1991	Wheal Jane mine formally abandoned
16 Nov 1991	Limited pumping to the Clemows Valley Tailings Dam started
17 Nov 1991	First release of minewater from Jane's adit into the River Carnon following groundwater rebound
4 Jan 1992	Emergency pumping stopped due to bad weather
13 Jan 1992	Nangiles plug burst – release of metalliferous minewater into the Fal Estuary
1992 – 1993	Temporary minewater treatment plant installed
1992 – 1998	Consultancy studies: Including feasibility and long-term strategy generation
Nov1998 – Mar 1999	Tender process for construction of minewater treatment plant
Jan 1999	Wheal Jane active minewater treatment trials
Sept 1999 – Mar 2000	Design of new active treatment plant
Mar 2000	Construction of Wheal Jane active minewater treatment plant
Oct 2000	Wheal Jane minewater treatment plant started operations
May 2001	Formal opening of Wheal Jane minewater treatment plant

The Wheal Jane mine (Wheal coming from the Celtic word 'huel', a work or mine, and Jane likely to have been either the landlords wife's name or daughter of the mine captain) has operated under various names, including Wheal Jane, Falmouth Consolidated, Wheal Whidden, Nangiles and Wheal Tremayne, over the centuries.

Mining operations have been intermittent at Wheal Jane during the centuries, largely due to high volumes of water entering the mine and, hence, high costs to dewater the mine. During the 'electric boom' of 1906, mining recommenced,

however due to the complex nature of the principal loads coupled with dewatering problems, the mine was closed in 1913.

In the 1960's, two new deep shafts were sunk, Clemows and No 2 shaft, to depths of 514m and 367m respectively. In 1976, the Mount Wellington mine was opened in the Carnon Valley, and became linked to the Wheal Jane mine underground.. Due to poor ore quality and severe dewatering problems, the Mount Wellington mine closed in 1978. This put extra dewatering demands on the Wheal Jane mine (the dewatering capacity was approximately 200 l/sec) and caused a brief closure of the Wheal Jane mine.

In 1979, both mines where taken over and operated as a single mine, however, acidic waters caused extensive corrosion to underground workings during the brief closure. Due to the world tin market collapse in the late 1980's, the price of tin dropped from close to £11,000 to just over £2,000 a tonne (Younger *et al.*, 2005). At this point, mining at Wheal Jane was uneconomic, and in February 1991 (after a further three changes in ownership), mining stopped at Wheal Jane. On the 9th September 1991, the mine was formally abandoned.

4.1.5 Discharge of Minewater into the Local Catchment

After underground operations ceased and the dewatering pumps were switched off in March 1991, the water level in the mine rebounded. By early September 1991, it was apparent that if treatment was not installed, an uncontrolled discharge of acidic minewater would take place. The National Rivers Authority (NRA), in conjunction with the mine owner, installed emergency lime treatment, dosed down Clemows shaft, and pumping of minewater from Clemows shaft to the Clemows Valley Tailing Dam (CVTD) (Figure 4.1), which was still receiving mill waste, as the ore from the South Crofty mine was being processed in the Wheal Jane Mill. On the 17th November 1991, the first release of minewater issued from Jane's Adit (Figure 4.1). This was plugged during November 1991.

During the wet winter of 1991-1992, the emergency treatment and pumping continued until the 4th of January 1992, when bad weather was affecting the treatment and settlement in the CVTD, resulting in a high turbidity in the discharge waters. On the 13th January 1992, an uncontrolled release of minewater occurred from Nangiles Adit (Figure 4.1). This was estimated to be between 25,000 and 50,000 m^3 of acidic minewater laden with metalliferous wastes. Initially the failure

of a plug on the Nangiles Adit (NRA, 1994; Bowen *et al.* 1998) was thought to have been the reason for this. However, more recently (Younger *et al.*, 2005), it is understood that there was no plug on Nangiles Adit and the sudden release was likely to have been caused by a failure in a pile of roof pile debris, which had been stopping the release of minewater from the adit.

The minewater released contained iron, zinc, cadmium, arsenic, plus other traces of toxic metals. Concentrations of dissolved metals peaked at 5000 mg/l and a very acidic pH of 2.5, due to the sulphides within the rocks. The European Community (EC) Environmental Quality Standards (EQS) in the River Carnon for zinc was exceeded by 900 times and similarly for cadmium by 600 times, Table 4.2. Figure 4.2 shows the cadmium and zinc concentrations present in the River Carnon from November 1991 to May 1992.

Table 4.2: Peak metal concentrations measured in the Carnon River on 14 Jan 1992 (Knight Piesold & Partners, 1999)

Determinant	Peak concentration (total metals, μg/l)	EC dangerous substances directive – fresh water EQS (total metals, μg/l)
pH	3	6-9
Arsenic	6,000	50 (dissolved)
Cadmium	600	1
Copper	7,000	28 (dissolved)
Iron	600,000	1,000 (dissolved)
Nickel	1,200	200 (dissolved
Zinc	440,000	500

Extensive monitoring was commenced immediately, undertaken by the Institute of Hydrology, covering the following 18-month period (Neal *et al.*, 2005). The results of the monitoring formed part of the consultancy studies undertaken by the Environment Agency (Knight Piesold & Partners, 1999).

As the oxidation products were flushed out of the mine, the minewater quality gradually improved with time, with this improvement presented in Figure 4.3.

The orange plume (Figures 4.4, 4.5 and 4.6), formed from the precipitation of Fe (III) hydroxide as the acid waters were neutralised by the saline tidal waters, stretched over 6.5 million m^2 (Brown *et al.*, 2002) of coastline, well known for to the fishing industry and tourism.

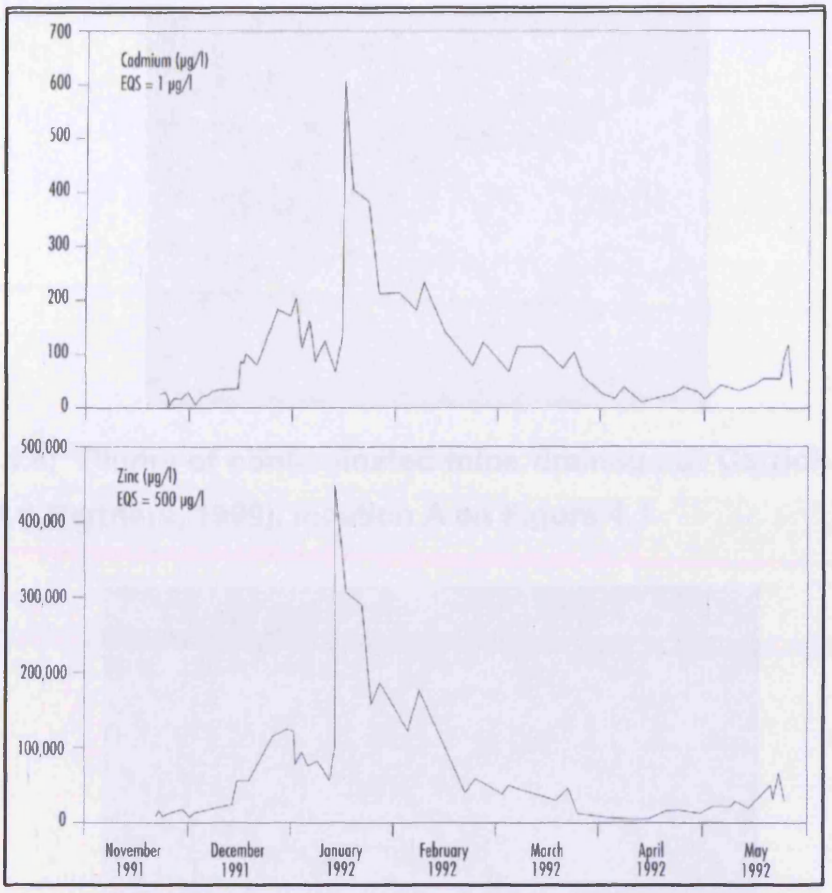


Figure 4.2: Zinc and cadmium concentrations in the River Carnon (November 1991- May 1992) (Knight Piesold & Partners, 1999)

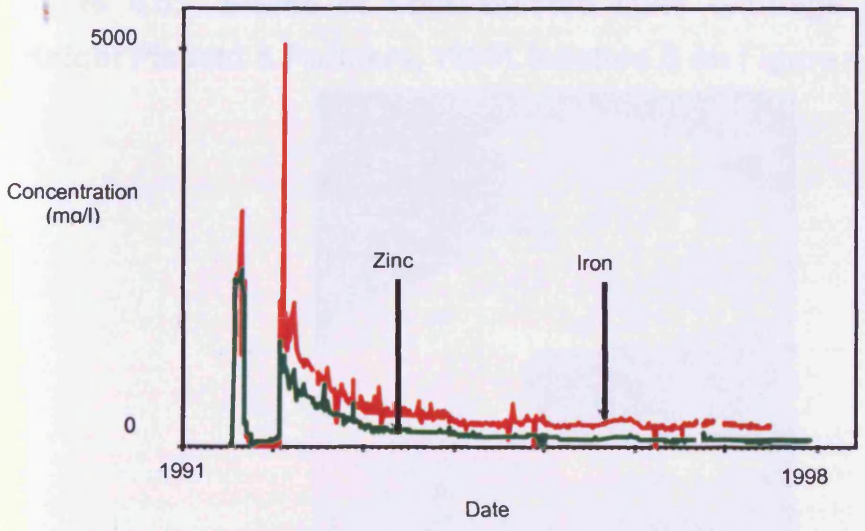


Figure 4.3: Decline in concentrations of iron and zinc in raw minewater discharged (naturally or pumped) from the Wheal Jane mine, 1991-2003 (EA data)

Figure 4.4: Plume of contaminated mine drainage at Carrick Roads (Knight Piesold & Partners, 1999), location A on Figure 4.1.

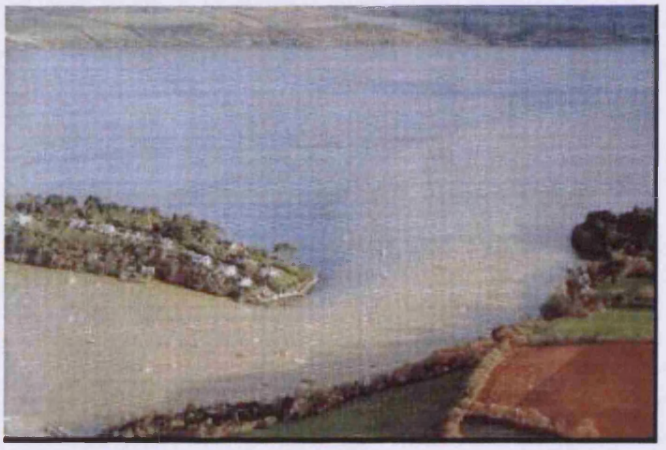


Figure 4.5: Plume of contaminated mine drainage entering Fal waters (Knight Piesold & Partners, 1999), location B on Figure 4.1.

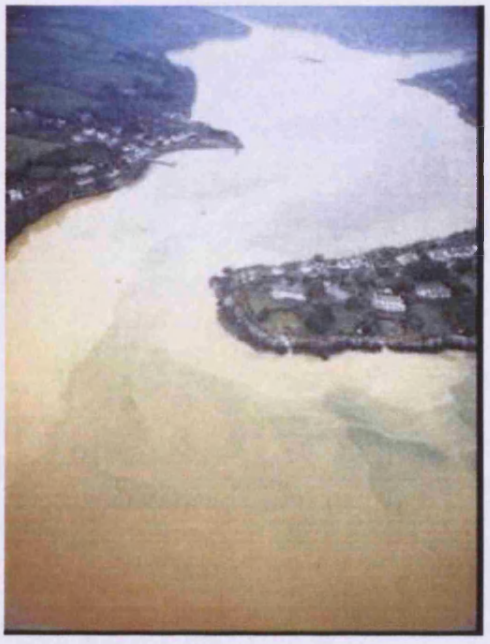


Figure 4.6: Plume of contaminated mine drainage passing Pandora Inn (see Figure 4.1), (Knight Piesold & Partners, 1999), location C on Figure 4.1.

4.1.6 Environmental Impact of the Discharge

The effects of the release of Wheal Jane acid minewater in January 1992 was extensively investigated, along with the development of a long-term treatment strategy by the Environment Agency (Knight Piesold & Partners, 1999). However, due to the already impoverished condition of the River Carvnon, the release had minimal impact on the environment and had no long term effect on the the flora and fauna in the River Carnon.

The most noticeable impact within the estuary was the discoloration of the sea, as shown in Figures 4.4, 4.5 and 4.6. This caused a perception problem with the general public, resulting in a perceived threat to the ecology of the estuary, to the fishing industry, to tourism and to the harvesting of a calcified seaweed, "maerl", in the estuary.

4.2 Temporary Treatment System

The emergency treatment plant was upgraded and was used temporarily until a long-term treatment strategy was developed. The temporary treatment system (shown schematically in Figure 4.7) included upgraded minewater pumps, a new head tank (where lime was dosed into the minewater), two new lime silos and batching tanks, a flocculation dosing system, and use of the CVTD (Figure 4.8) for settlement and sludge depository and a new polishing lagoon at the base of the CVTD. The treated water was discharged to the Clemows Stream.

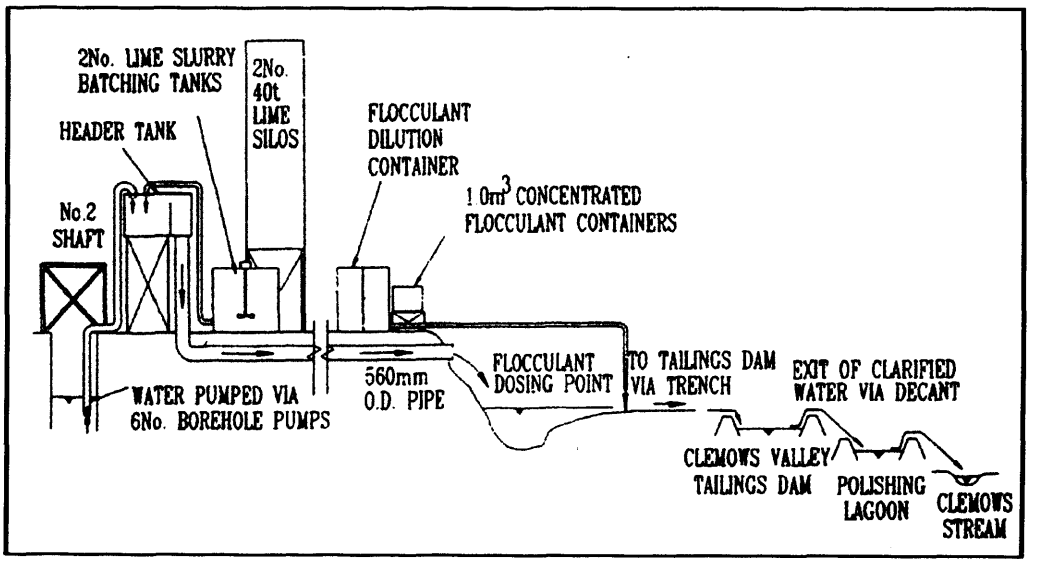


Figure 4.7: Temporary Wheal Jane Treatment Plant (Cambridge, 1997)

Figure 4.8: Clemows Valley tailings dam (Knight Piesold & Partners, 1999)

4.3 Long-term Treatment Selection and Appraisal

The temporary treatment plant gave the Environment Agency time to commission consultants to undertake consultancy studies on the impact of the discharge and to assess long-term treatment options (Cambridge, 1997; Hallett *et al.*, 1999). These studies showed that passive treatment was not appropriate as there was insufficient suitable land available within the Carnon Valley to reliably treat the Wheal Jane Minewater.

The studies reviewed a variety of technologies and concluded that conventional oxidation and chemical neutralisation (OCN), biochemical sulphidisation (BCS) and ion exchange (IEX) were the most appropriate treatment methods. The project team identified that the disposal of sludge was a significant component of the project cost and therefore it was crucial to minimise the volume of sludge generated. Preference was therefore given to either a lime-based High Density Sludge (HDS) process or sulphide precipitation (although concerns were raised about the long-term storage of sulphide rich sludge).

The Environment Agency (EA) and The Department of Environment Transport and the Regions (DETR) developed a procurement strategy for the appointment of a contractor to design, build and operate (DBO) the plant for a period of 10 years. To achieve these objectives within the EU Procurement Procedure, framework contractors were pre-qualified and invited to tender on the basis of either an illustrative design prepared by the EA consultants or their own preferred treatment

technology. The tenders were evaluated on the basis of the technology offered, project costs and risk. A preferred contractor was selected to take the project forward in an open book contractual arrangement that used the tender prices as the basis for developing the final scheme cost.

The contract was tendered between November 1998 and March 1999. As part of its tender bid, United Utilities Industrial (UUI) engaged Camborne School of Mines Associates (CSMA) to identify technologies capable of meeting the Agency's requirements for the Wheal Jane Minewater Treatment Plant (McGinness *et al.*, 1998). CSMA identified five suitable technologies, of which the Type II HDS process, designed by Unipure Europe Ltd (Monmouth, Wales), was deemed the most appropriate. UUI was appointed as the preferred contractor in May 1999 and a finalised project target cost was agreed in September 1999.

4.4 Wheal Jane HDS Minewater Treatment Plant

The long-term active Wheal Jane HDS Minewater Treatment Plant (MWTP) is a Type II HDS Process (see Section 2.10). The following sections detail the design and the first two years operation and performance, with a summary of the data being found in Coulton *et al.*, 2003b. The data generation and collection were managed by the author as part of the plant management, for which the author was responsible during the first two years of operation.

4.4.1 Pilot Plant Trials

To assess the performance of the Type II HDS process, pilot plant trials were undertaken in January 1999 and August 1999. The results of the first campaign demonstrated the suitability of the Type II HDS process. The second set of trials were used to optimise the design and estimate the long-term operational costs.

4.4.2 Design Specification

The flow from the mine varies seasonally, typically peaking in excess of 330 l/sec during January to March and declining to about 110 l/sec during August to September. To accommodate this range, it was decided to install two identical treatment streams, each with a rated capacity of 230 l/sec (with the ability to treat the minewater delivered by four pumps, together with the seepage water recovered from the toe of the CVTD). For an average year, both streams are only

expected to operate for around seven months per year, allowing essential maintenance to be carried out during the remainder of the year.

The predicted 10-year minewater quality is presented in Table 4.3 (Environment Agency, 2000), together with the short-term (Phase I) and long-term (Phase II post 1st March 2002) discharge consents.

Table 4.3: Wheal Jane MWTP water quality requirements

(Environment Agency, 2000),

	Minewater		Discharge Consent	
Parameter	**Average (mg/l)**	**Maximum (mg/l)**	**Short-term (mg/l)**	**Long-term (mg/l)**
pH (pH units)	3.50	3.85	6-10	6.5-10
Total As	3.0	16.0	0.5	0.1
Total Al	23.0	40.0	13.0	10.0
Total Cd	0.056	0.149	0.04	0.04
Total Cu	0.80	7.65	0.3	0.08
Total Fe	206	402	5.0	5.0
Total Mn	6.0	19.2	7.0	1.0
Total Ni	0.55	1.2	1.0	1.0
Total Zn	51.0	176.0	20	2.5
Total Pb	0.15	0.60	-	-

The compliant design required the installation of tertiary sand filters to ensure satisfactory final effluent suspended solids and manganese concentrations, together with a filter press to dewater the sludge to at least 50% (w/w) solids. The pilot trials indicated that a satisfactory final effluent quality could be achieved without the use of sand filters and that the sludge settled rapidly to about 35% (w/w) solids within 8 hours. Filter press trials demonstrated that solids concentrations in excess of 70% (w/w) could be achieved using either conventional or membrane presses. Based on these results, potential savings of up to £2M were identified in the capital cost by not installing the tertiary sand filters or the sludge press.

It was therefore decided to construct the plant in two phases comprising:

- Phase I - Reaction vessels and sludge clarifier/thickeners, with the direct discharge of treated effluent to river, and surplus sludge pumped to the CVTD for settlement and storage.

- Phase II - tertiary filters and sludge press.

To confirm whether the tertiary filters and the sludge press were needed, it was decided to delay the Phase II works for 12 months to allow the performance of the full scale Phase I plant to be assessed. To allow UUI to operate the plant during this period, the EA granted a less onerous short-term discharge consent (Table 4.3).

4.4.3 Design Parameters

Based on the pilot plant trials, the MWTP was designed on the parameters presented in Table 4.4 (Hyder Industrial Limited, 1999).

Table 4.4: Wheal Jane HDS MWTP design parameters

(Hyder Industrial Limited, 1999)

Reactors parameters	**Stage 1 Reactor Values**	**Stage II Reactor Values**
Minimum retention time	30 min	30 min
Sludge recirculation ratio	25:1 to 50:1	
Operating pH	6.5- 7.5	9.25
Lime efficiency		69% utilisation
Clarifier parameters	**Clarifiers Values**	
Clarifier rise rate	1.2 $m^3/m^2.hr$	
Clarifier loading rate	2.0 m^2/tph	
Flocculant dosing rate	3.0 mg/l	
Recirculation sludge density	20 % w/w	

4.4.4 Plant Layout

The plant layout is shown in Figure 4.9 and is illustrated schematically by the author in Figure 4.10. Each stream is identical and consists of a Stage I Reactor, a Stage II Reactor and two lamella clarifiers. Both streams are served by common equipment, comprising lime and flocculant make-up systems, air blowers, a sludge holding tank, transfer pumps and final effluent discharge monitoring equipment.

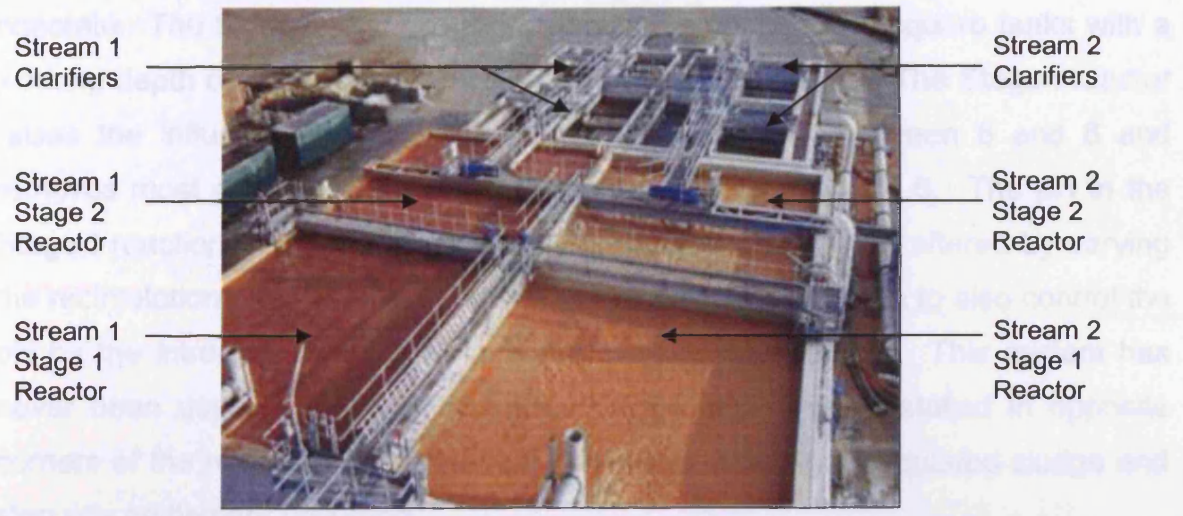


Figure 4.9: Photograph showing the general layout of the Wheal Jane MWTP (Note: Stream 1 is on the left and Stream 2 is on the right)

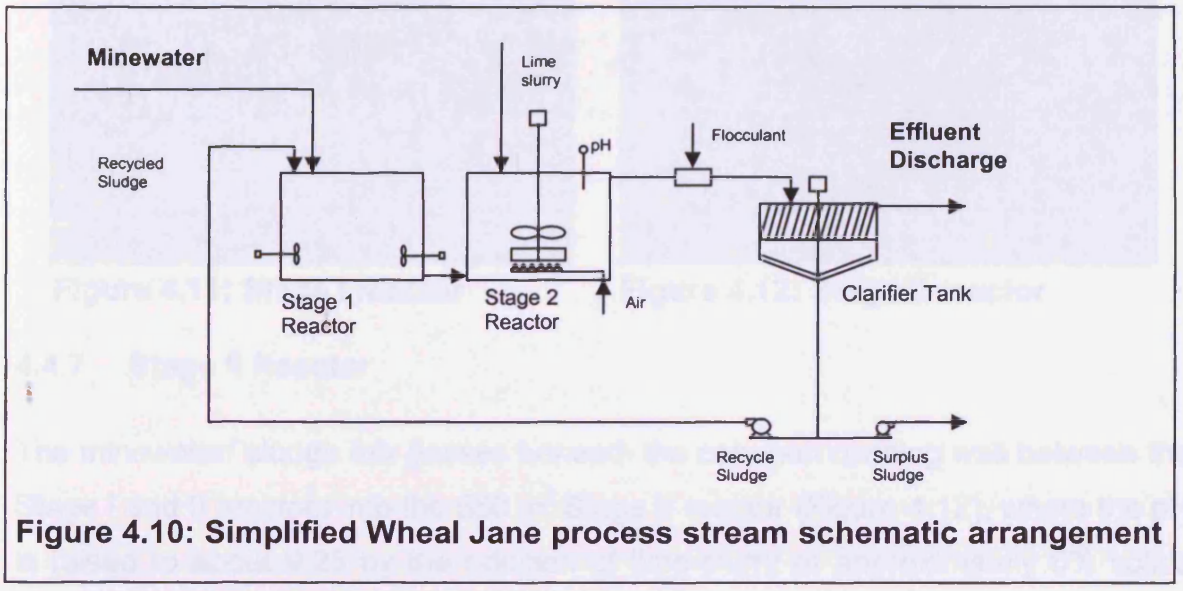


Figure 4.10: Simplified Wheal Jane process stream schematic arrangement

4.4.5 No 2 Shaft Borehole Pumps

Raw minewater is lifted some 65 m from No 2 Shaft into the plant by 6 three-stage Grundfos (SP215) submersible pumps, each delivering up to 55 l/sec. A standby pump is permanently installed in the shaft for immediate use with an eighth pump held in store. The pumps (and associated power cable) are supported by 150 mm diameter Wellmaster pipe connecting the pumps to a flow distribution manifold located at surface level.

4.4.6 Stage I Reactor

The raw minewater is initially treated by the recirculated sludge in the Stage I reactor (Figure 4.11). The reactors and the clarifier tanks are constructed from

concrete. The Stage I (and Stage II) reactors comprise 10 m square tanks with a working depth of about 5.5 m and working capacity of 550 m^3. The Stage I reactor raises the influent minewater pH from 3.5, to a pH of between 6 and 8 and removes most of the dissolved metals out of solution, Table 4.6. The pH in the Stage I reaction chamber is not directly controlled, but can be altered by varying the recirculation rate. Provision was made in the original design to also control the pH by the introduction of lime via a manually operated valve. This system has never been used. Two 4 kW Landia POPR-I mixers are installed in opposite corners of the reactors to mix the raw minewater with the recirculated sludge and stop any settlement occurring.

Figure 4.11: Stage I reactor

Figure 4.12: Stage II reactor

4.4.7 Stage II Reactor

The minewater/ sludge mix passes beneath the common dividing wall between the Stage I and II reactors into the 550 m^3 Stage II reactor (Figure 4.12), where the pH is raised to about 9.25 by the addition of lime-slurry at approximately 6% solids (wt/wt). The operational pH is controlled between 9.15 and 9.35 to ensure that the total manganese concentration of the final effluent complies with the discharge consent. Air blowers are used to introduce oxygen to ensure complete oxidation of Fe (II) to Fe (III). A Mixertech type 1163 mixer, driven by a 75 kW motor via a Flender B3BV09, is used to ensure satisfactory oxygen transfer and adequate mixing. The mixers are fitted with a bottom mounted vertical blade turbine and a propeller type impeller. The vertical blade turbine provides sufficient shearing energy to break up any weak sludge particles and to enhance the rate of oxygen transfer from air introduced by the sparge system. The impeller breaks up the coarse air bubbles produced by the sparge pipe into much smaller bubbles, which, due to greater surface area, increases the oxygen transfer rate by at least 300%. To ensure adequate mixing, a propeller type impeller is located about 1/3 of the

way up the submerged length of the shaft.

The pH and solids levels within the Stage II reactor are monitored by Endress & Hauser probes which are used via the PLC to control the Stage II reactor pH.

4.4.8 Inline Static Mixer

The minewater/ sludge mixture passes from the Stage II reactors, through an inline static mixer (Statiflo series 600 motionless mixer), where a slightly anionic flocculant (Magnafloc 155, supplied by Ciba Specialist Chemicals, Bradford, UK) is added to assist solid/liquid separation. The dosed mixture then flows through a launder into each of the clarifiers.

4.4.9 Lamella Clarifier/Thickener Units

Solids/liquid separation is achieved in two 7 m^2 lamella clarifier/thickener units operated in parallel. Thickened solids from the clarifier are either recirculated to the Stage I reactor or are surplused from the system at a solids concentration of between 15 and 25% (w/w). Lamella packs were installed in each unit to increase the effective clarification area of each unit from 49 m^2 to about 400 m^2. Thickened sludge is recovered from the base of the clarifier via a 150 mm diameter underflow pipe connected to the sludge recirculation and surplusing pumps (4 kW Warman 100 C-GP and 1.5 kW Warman GP75B-CCC-A1 respectively). Sludge is directed to the centrally positioned underflow pipe by a rake mechanism driven by 1.1 kW motors. The volume of sludge returned to the Stage I Reactor is automatically varied in response to changes in the minewater flow rate. A magnetic flowmeter (Danfoss Magflow type 5000) located on the sludge return line is used to control the speed of the variable speed recirculation pump, thereby ensuring that the required flow rate is pumped irrespective of the sludge viscosity. An Endress & Hauser Probfit CUA461 sludge density meter is fitted to each sludge recirculation line to monitor the underflow solids concentration. These are used to automatically excess sludge once the solids content exceeds a predetermined value.

4.4.10 Sludge Surplusing

Excess sludge from the plant is pumped to a 368 m^3 holding tank, designed to provide at least 5 days sludge storage capacity. Two Landia mixers prevent

settlement within the tank. Warman centrifugal pumps automatically pump the sludge from the tank to the CVTD (Figure 4.13), where the solids settle and consolidate to about 50% w/w.

Figure 4.13: Clemows Valley tailings dam, with paddocks

4.4.11 Final Effluent Monitoring

Clarified overflow is collected in a central launder, Figure 4.14, prior to final effluent monitoring. The volume of treated water discharged from the plant is measured using an ultrasonic level meter (Pulsar Flow Oracle) and 'V' notch weir. In addition, the final effluent solids content is measured using an Endress & Hauser turbidity meter and the pH is triple validated by three Endress & Hauser pH probes. All the final effluent validation data are automatically recorded and used for discharge compliance and process control.

Figure 4.14: Wheal Jane MWTP clarifier overflow

4.4.12 Lime Make-up System

The original lime make-up system, installed in 1993, is used to supply lime slurry

to the MWTP. The system is capable of storing 80 tonnes of calcium hydroxide in two 40 tonne silos. Lime slurry was originally supplied alternately from two batch tanks. However, as part of the HDS plant installation, this was modified to transfer the batched lime-slurry to a holding tank, from where it is pumped by a Warman centrifugal pump around the plant. The lime dosing into the Stage II reactors is controlled by means of a PID controller using an Endress & Hauser pH meter and Rotork actuated valves.

4.4.13 Polymer Make-up System

A Ciba Specialist Chemicals Ltd flocculation preparation unit is used to make up powder flocculant into a 0.35% w/v solution for flocculation purposes. The flocculant preparation plant is common to both streams, being fed by two sets of dosing equipment, one set up per stream. Following a number of jar and plant optimisation trials, a slightly anionic flocculant is used (Magnafloc 155). This was originally being dosed at 3 mg/l, but was subsequently reduced to 1.6 mg/l without adversely affecting water quality.

4.4.14 Air Blower System

Each process stream has two Hick Hargreaves air blowers (rated at 30 kW and 15 kW), providing up to 2664 m^3 of air per hour. A third 30 kW unit is installed as a common standby.

4.4.15 Instrumentation, Control and Automation (ICA)

The plant is automatically controlled by an Allen Bradley PLC (programmable logic controller). All levels, flows and meter readings are recorded, together with the operational state of every major component. Access is gained to the PLC by a SCADA system, which also records all historical activities. The plant operational state is monitored by a telemetry system.

Data from the final effluent flow and quality monitors is also sent to the Environment Agency's regional control centre, from where the performance of the plant can be independently verified.

4.4.16 Operational Performance of Phase I Plant

Commissioning of the Phase I plant took place in October 2000. High density

sludge was formed within two days of flows being turned on and effluent was discharged directly to the environment, without using the tailings dam as polishing facility, within 4 days. Throughout the month of December 2000, 344 l/sec of minewater was treated by the plant. The average effluent quality (Table 4.5) over the first 24 months was 0.79 mg/l iron, 0.20 mg/l zinc and 0.32 mg/l manganese. As a result of the plant performance, tertiary treatment was not installed. The optimisation of the plant resulted in a reduction in the flocculant dose rate from 3 mg/l to 1.6 mg/l in September 2002, and a reduction in power consumption.

4.4.17 Phase II Plant Upgrade

A performance review of the plant was undertaken after a period of 12 months operation. This confirmed that the plant performance had exceeded expectations, with very low residual metal and solids concentrations in the treated minewater. In addition, the settlement characteristics of the sludge were such that the target density of 50% (w/w) solids (unpublished EA data) could be achieved in the dam without the use of sludge dewatering. Following this review, it was decided that installation of the tertiary filters was not necessary to meet the required solids concentrations in the treated minewater, but that the robustness of the operation would benefit from the installation of a new lime plant control panel, the installation of a large lime-slurry storage tank and the provision of a standby flocculation system. In addition, to minimise the risk to the environment in the event of plant failure, provision was made to use the CVTD as an emergency storage facility.

The net saving achieved as a result of not installing the tertiary filtration and the sludge filter press was estimated to be £1.7M.

4.5 Wheal Jane MWTP Plant Data Review

4.5.1 Introduction

Minewater was first pumped through the Wheal Jane MWTP on the 28th September 2000, when plant commissioning started. The plant was 'handed over' at the end of October 2000. This review summarises the data generated between 1st October 2000 and 30th September 2002, where data is available.

During the period 1st October 2000 and 30th September 2002, Wheal Jane MWTP treated an average of 17,227 m^3/day of minewater, with a maximum of 35,772

m^3/day. This equated to a total minewater flow of approximately 12.4 $x10^6$ m^3. In addition to minewater, dam toe drain (and dam supernatant water) flows were treated at an average flow of 306 m^3/day, with a maximum of 2,352 m^3/day.

The operating pH of the Stage II reactor was set at 9.25.

4.5.2 Plant Water Quality

Water quality samples of the minewater and treated water were regularly taken for analysis. A summary of the results from the analysis are presented by the author in Table 4.5.

Table 4.5: Wheal Jane MWTP Average minewater and treated water concentrations (Oct 2000 to Sept 2002)

Determinant	Minewater			Discharge		
	Min (mg/l)	Average (mg/l)	Max (mg/l)	Min (mg/l)	Average (mg/l)	Max (mg/l)
Cadmium	0.006	0.027	0.300	0.001	0.001	0.011
Copper	0.01	0.30	3.40	0.01	0.01	0.10
Zinc	0.60	44.36	60.00	0.01	0.20	3.90
Iron	134.0	191.1	256.0	0.01	0.79	3.10
Nickel	0.30	0.43	6.40	0.01	0.10	0.40
Aluminium	11.6	12.3	13.7	0.3	0.7	1.1
Manganese	4.30	5.76	7.10	0.09	0.32	5.20
Arsenic	2.00	6.77	12.50	0.01	0.10	0.11
Calcium	59.2	97.9	296	99.6	311.7	565
Magnesium	12.0	13.4	18.4	7.0	8.43	15.2
Sulphate	590	741	911	273	723	876
Solids	1.50	6.63	37.0	1.5	6.2	14.9
pH (pH units)	2.2	3.5	4.70	7.1	8.7	9.2

The minewater concentrations showed seasonal variations as predicted. During November 2000, shortly after 'hand over', operational difficulties were experienced with the Stage II reactor pH probes and resulted in the only measured occasion of the treated water being above the consented limit. The frequency of calibration of the pH probes was increased, which resolved the issue. In the 2 years of operation, the Environment Agency did not detect a discharge consent breach during routine consent compliance monitoring.

During May 2002, a series of stage samples were taken from Stream 1 and analysed for various determinants to investigate where the dissolved metals are

removed from solution. A summary of these results is presented by the author in Table 4.6. This shows that the majority of metal precipitation occurs in the Stage I reactor, the exception being the precipitation of the manganese which is completed in the Stage II reactor. The data also show that approximately 28.3% of the solids is present as iron, approximately 12% is present as carbonates whilst only 2% is present as sulphates. This would indicate that the calcium in the sludge is predominately present as calcium carbonate with only a small amount present as calcium sulphate.

Table 4.6: Wheal Jane MWTP Summary of May 2002 stage sample results

Determinant	Minewater (mg/l)	Stage I reactor (mg/l)	Stage II reactor (mg/l)	Recirculation sludge (mg/l)	Discharge (mg/l)
pH (pH units)	3.7	7.8	8.9	8.9	8.7
Suspended Solids	3.4	13,500	13,800	97,400	4.2
Total cadmium	0.011	0.178	0.198	1.27	<0.001
Total copper	0.09	1.56	1.40	11.0	<0.001
Total zinc	46.5	762	765	5,430	0.1
Total iron	236	3,870	3,890	27,700	0.3
Total nickel	0.4	6.5	6.6	46.3	<0.1
Total manganese	6.48	117	120	857.0	0.32
Total arsenic	9.8	59.9	51.7	416	<0.1
Total calcium	125	1,190	1,250	8,880	393
Total sulphate	841	260	260	1,890	827
Chemically bound water	-	1,140	1,250	7,960	2.0
Total carbonate	-	1,620	1,510	11,900	11.0
Dissolved cadmium	0.009	<0.001	<0.001	<0.001	<0.001
Dissolved copper	0.07	<0.01	<0.01	<0.01	<0.01
Dissolved zinc	45.7	0.4	0.2	0.2	0.1
Dissolved iron	230	0.2	0.4	0.1	0.3
Dissolved nickel	0.4	<0.1	<0.1	<0.1	<0.1
Dissolved manganese	6.34	3.2	0.4	0.4	
Dissolved arsenic	9.4	<0.1	<0.1	<0.1	
Dissolved calcium	122	367	369	349	
Dissolved sulphate	820	793	808	784	
Chemically bound water	-	1.1	1.0	0.9	
Dissolved carbonate	-	16.3	8.3	6.8	

Note: aluminium analysis was not undertaken

4.5.3 Plant Flows and Reactor Retention Time

The stream total flow rates (stream flow and recirculation flow) are presented in

Figure 4.15. The average Stream 1 total flow was 587 m^3/hr (minewater flow and recirculation flows being 484 m^3/hr and 103 m^3/hr respectively), whilst the average Stream 2 total flow was 289 m^3/hr (minewater flow and recirculation flows being 241 m^3/hr and 48 m^3/hr respectively).

The reactor retention time has been calculated by using the total flow, i.e. reactor volume (m^3) divided by total flow through the stream (m^3/hr), instead of the conventional method of using just the feed flow. This was done to take into account the recirculation flow, as this also reduces the retention time in each reactor. The average Stream 1 reactor (Stage I and Stage II) retention time was 61 minutes and the average Stream 2 reactor (Stage I and Stage II) retention time was 75 minutes or 23% longer.

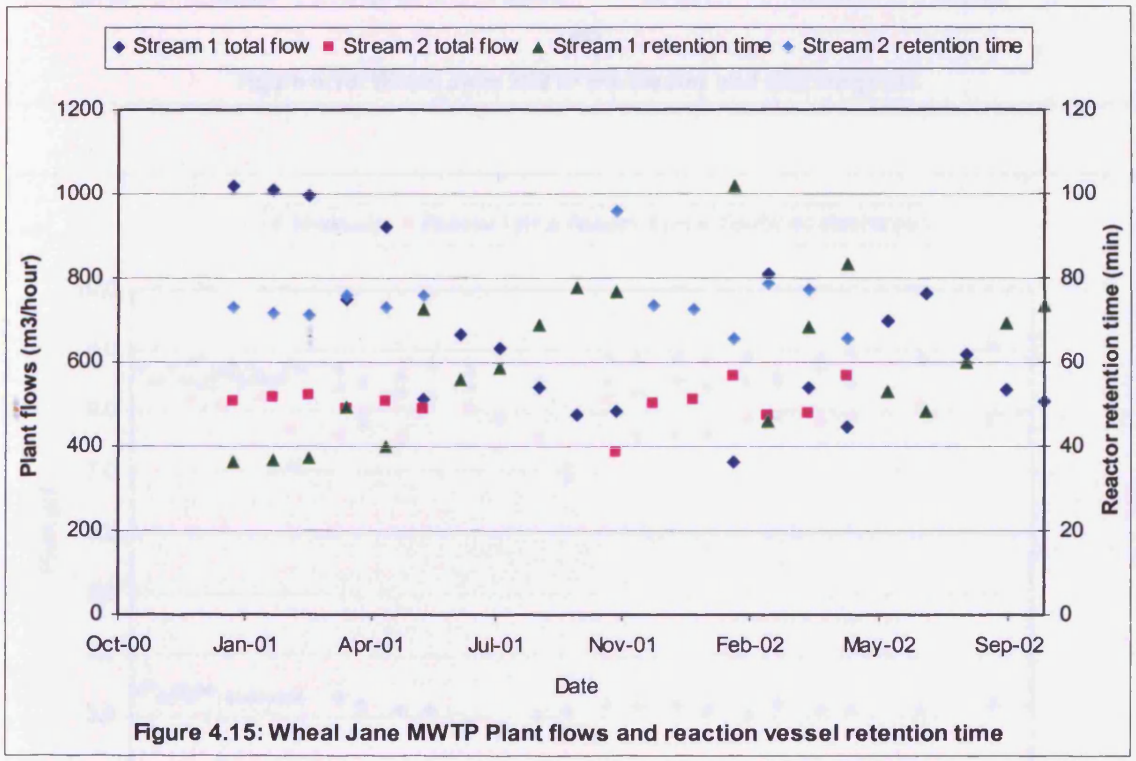


Figure 4.15: Wheal Jane MWTP Plant flows and reaction vessel retention time

4.5.4 System pH and Redox potential

Minewater and discharge pH throughout the review period are summarised in Figure 4.16. The average minewater pH was 3.2 and the average discharge pH was 8.7.

Presented in Figure 4.17 are the Stream 1 pH measurements during the period October 00 to January 01. This indicates that the average Stream 1 Stage I reactor and Stage II reactor pH measurements were 7.9 and 8.6 respectively.

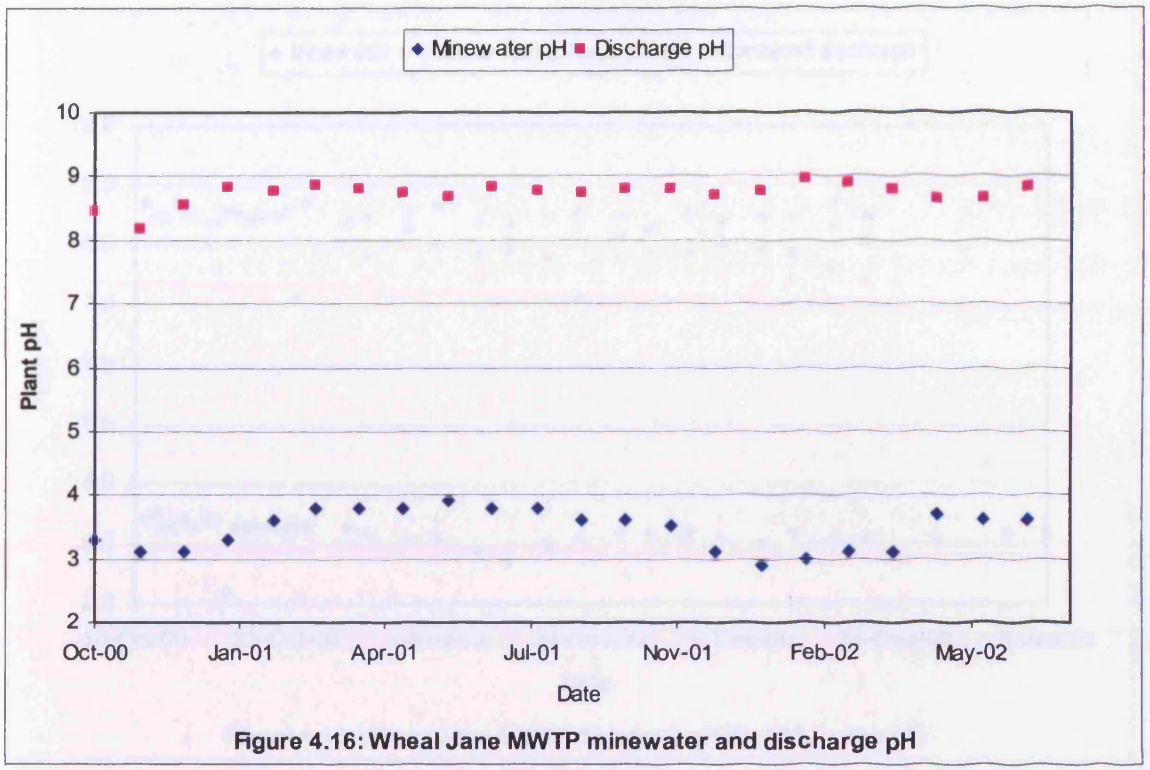


Figure 4.16: Wheal Jane MWTP minewater and discharge pH

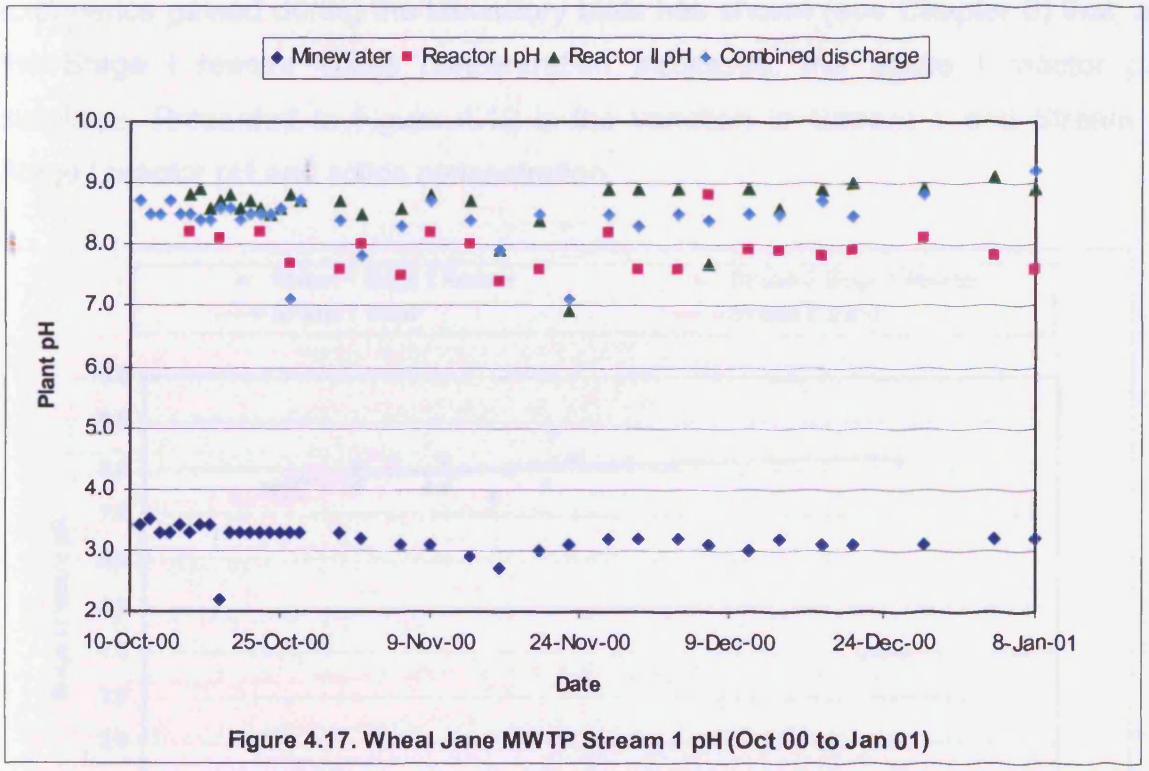


Figure 4.17. Wheal Jane MWTP Stream 1 pH (Oct 00 to Jan 01)

As a comparison to Figure 4.17, presented in Figure 4.20 are the Stream 2 pH measurements during the period October 00 to January 01. This figure indicates that the average Stream 2 Stage I reactor and Stage II reactor pH measurements were 7.7 and 8.3 respectively, i.e. Stream II operated at a slightly reduced pH compared to Stream I.

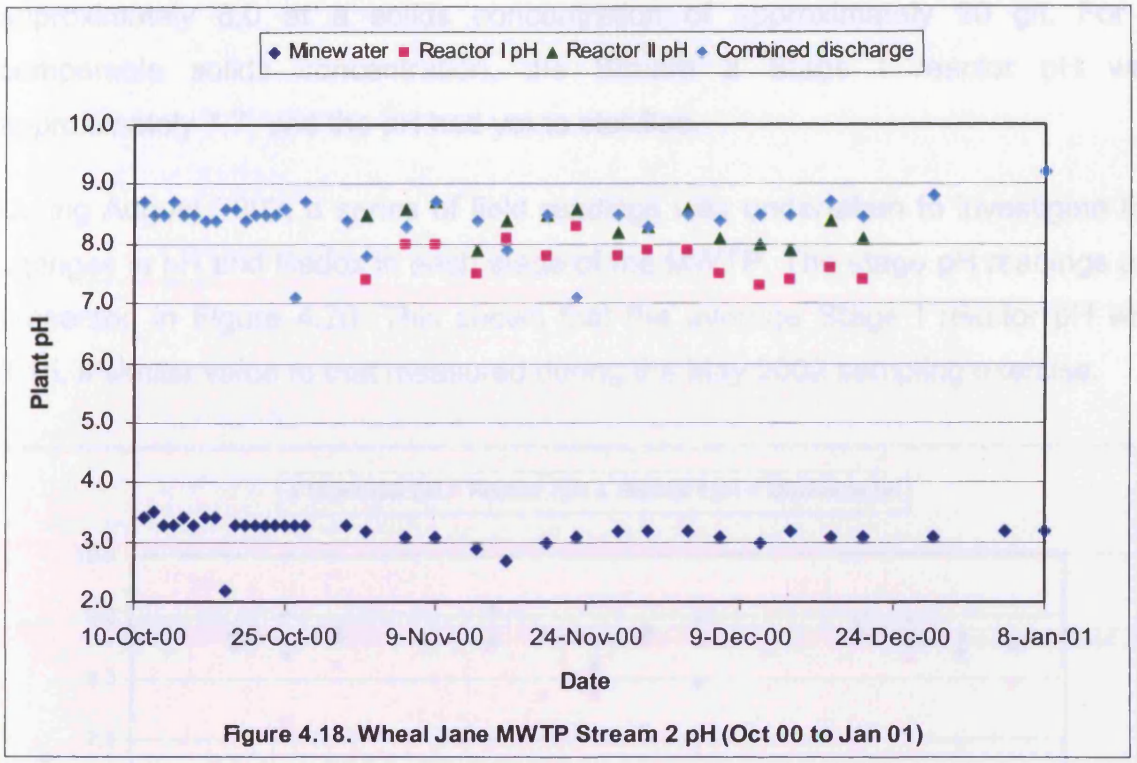


Figure 4.18. Wheal Jane MWTP Stream 2 pH (Oct 00 to Jan 01)

Experience gained during the laboratory trials has shown (see Chapter 6) that, as the Stage I reactor solids concentration increases, the Stage I reactor pH stabilises. Presented in Figure 4.19 is the variation in Stream 1 and Stream 2 Stage I reactor pH and solids concentration.

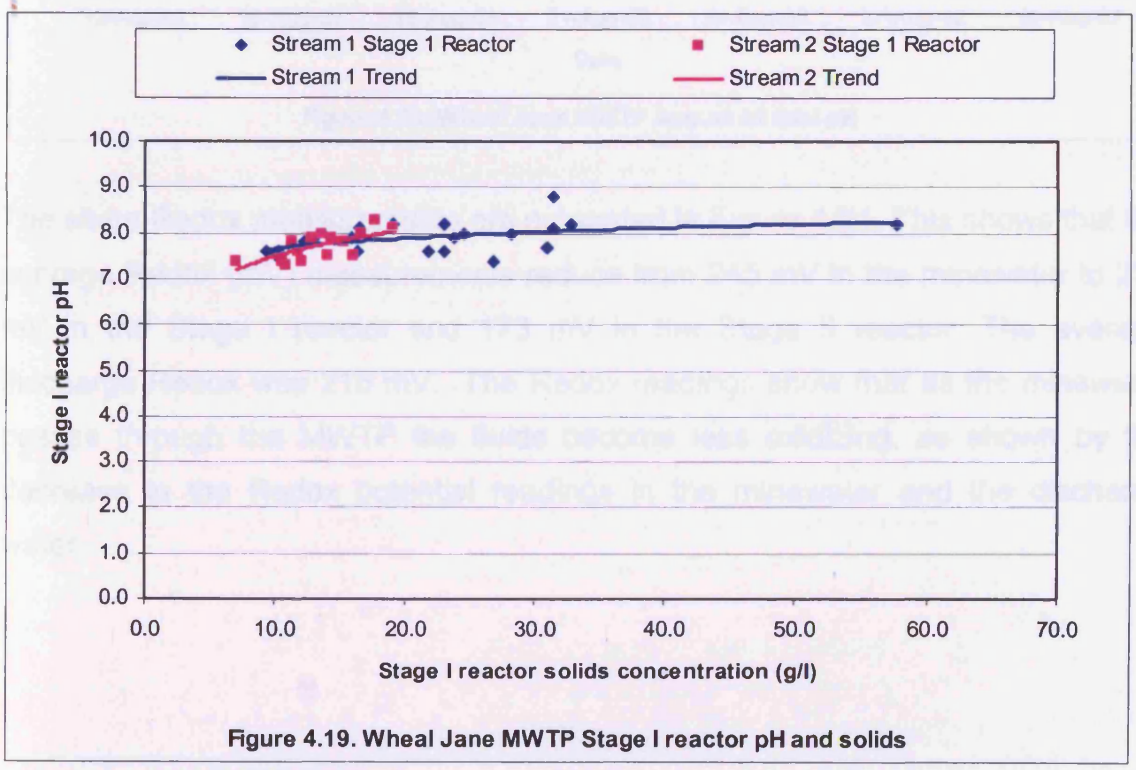


Figure 4.19. Wheal Jane MWTP Stage I reactor pH and solids

This suggests that the Stream 1 Stage I reactor pH stabilised at a pH of

approximately 8.0 at a solids concentration of approximately 20 g/l. For a comparable solids concentration, the Stream 2 Stage I reactor pH was approximately 7.7, and the pH had yet to stabilise.

During August 2002, a series of field readings was undertaken to investigate the changes in pH and Redox in each stage of the MWTP. The stage pH readings are presented in Figure 4.20. This shows that the average Stage I reactor pH was 8.15, a similar value to that measured during the May 2002 sampling exercise.

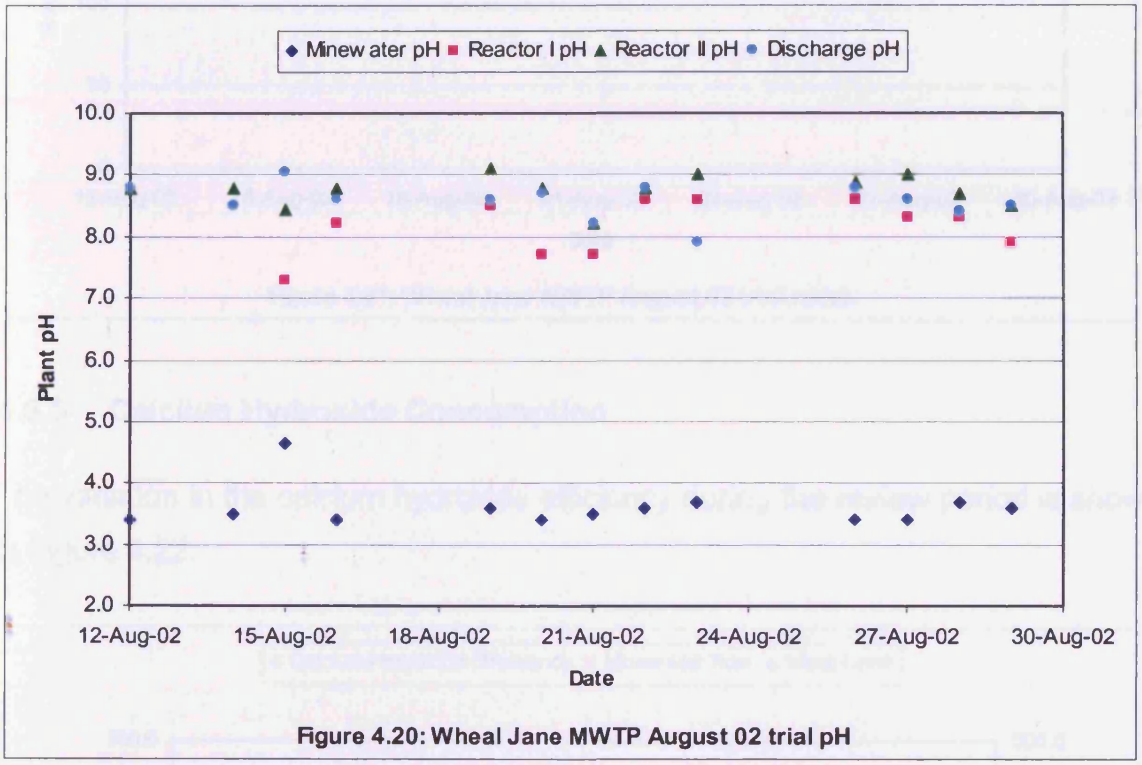


Figure 4.20: Wheal Jane MWTP August 02 trial pH

The stage Redox measurements are presented in Figure 4.21. This shows that the average Redox (mV) measurements reduce from 245 mV in the minewater to 207 mV in the Stage I reactor and 173 mV in the Stage II reactor. The average discharge Redox was 215 mV. The Redox readings show that as the minewater passes through the MWTP the fluids become less oxidizing, as shown by the decrease in the Redox potential readings in the minewater and the discharge water.

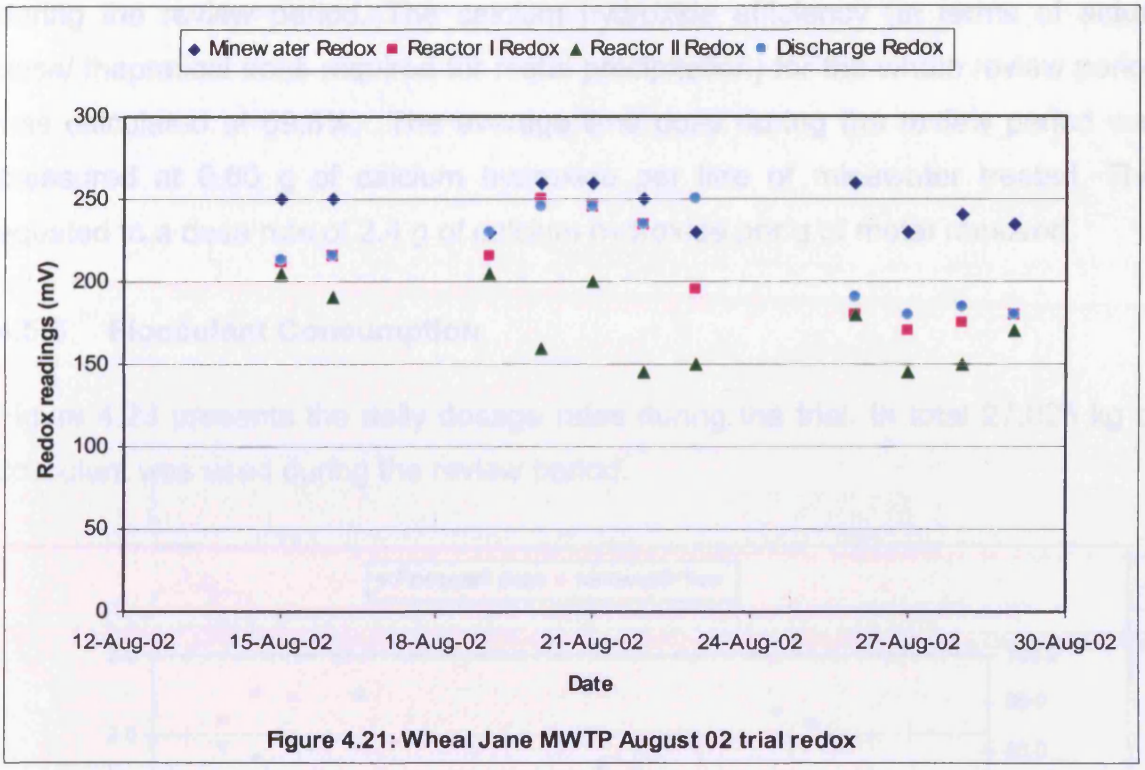


Figure 4.21: Wheal Jane MWTP August 02 trial redox

4.5.5 Calcium Hydroxide Consumption

The variation in the calcium hydroxide efficiency during the review period is shown in Figure 4.22.

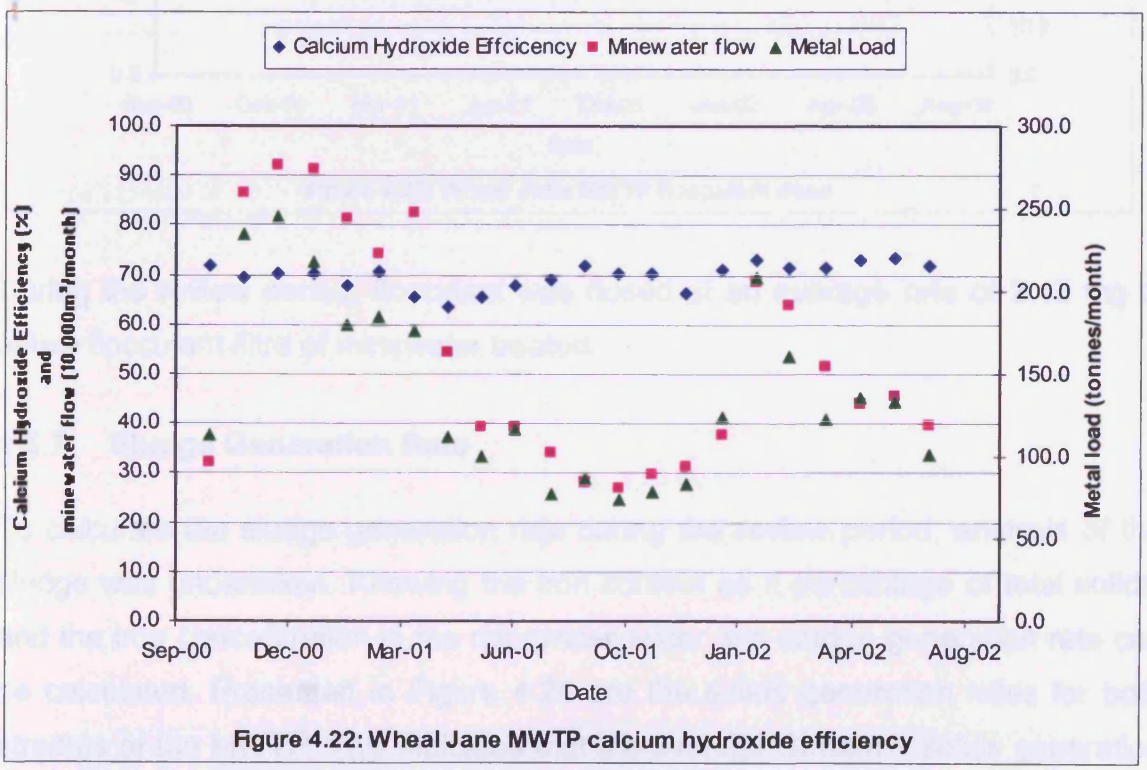


Figure 4.22: Wheal Jane MWTP calcium hydroxide efficiency

In total, 7,438 tonnes of calcium hydroxide were used in treating the minewater

during the review period. The calcium hydroxide efficiency (in terms of actual dose/ theoretical dose required for metal precipitation) for the whole review period was calculated at 69.8%. The average lime dose during the review period was measured at 0.60 g of calcium hydroxide per litre of minewater treated. This equated to a dose rate of 2.4 g of calcium hydroxide per g of metal removed.

4.5.6 Flocculant Consumption

Figure 4.23 presents the daily dosage rates during the trial. In total 27,025 kg of flocculant was used during the review period.

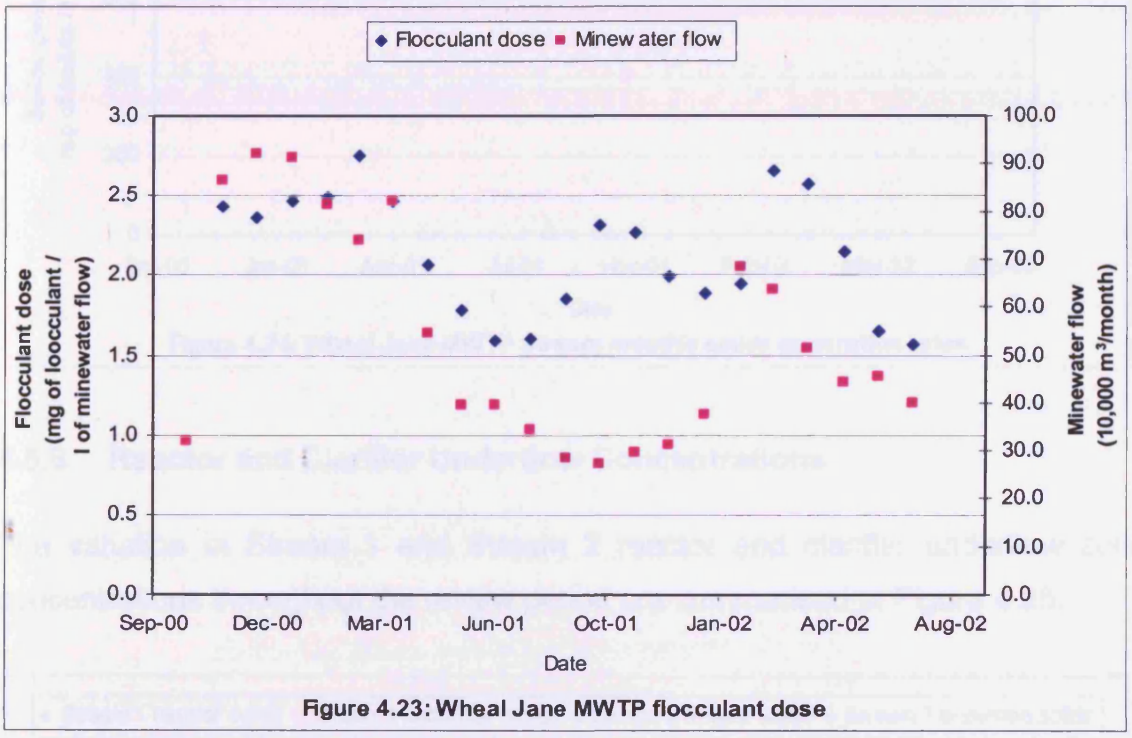


Figure 4.23: Wheal Jane MWTP flocculant dose

During the review period, flocculant was dosed at an average rate of 2.13 mg of active flocculant /litre of minewater treated.

4.5.7 Sludge Generation Rate

To calculate the sludge generation rate during the review period, analysis of the sludge was undertaken. Knowing the iron content as a percentage of total solids, and the iron concentration in the minewater water, the sludge generation rate can be calculated. Presented in Figure 4.24 are the solids generation rates for both streams of the MWTP. This indicates that the average Stream 1 solids generation rate was 762 mg of solids / l of minewater, and the average Stream 2 solids generation rate was 720 mg/l. Comparing the generation rates for when both

streams were operational simultaneously, the winter months, Stream 1 generated on average 6% more solids (747 mg/l for Stream 1 compared to 698 mg/l for Stream 2).

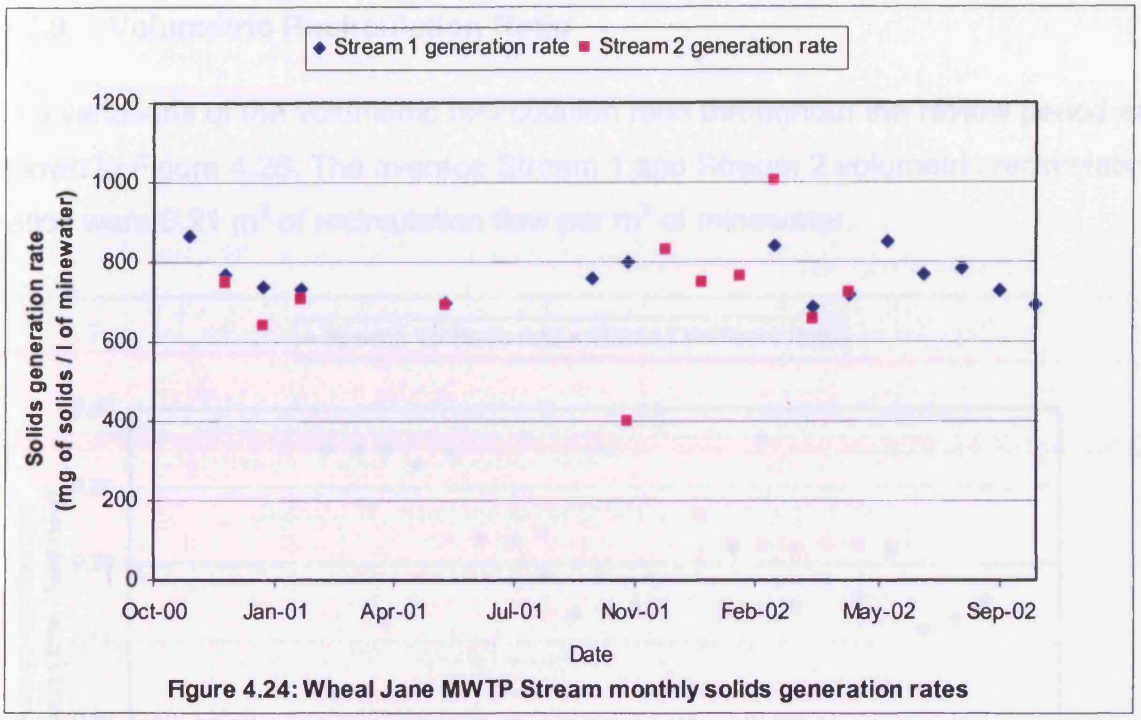


Figure 4.24: Wheal Jane MWTP Stream monthly solids generation rates

4.5.8 Reactor and Clarifier Underflow Concentrations

The variation in Stream 1 and Stream 2 reactor and clarifier underflow solids concentrations throughout the review period are summarised in Figure 4.25.

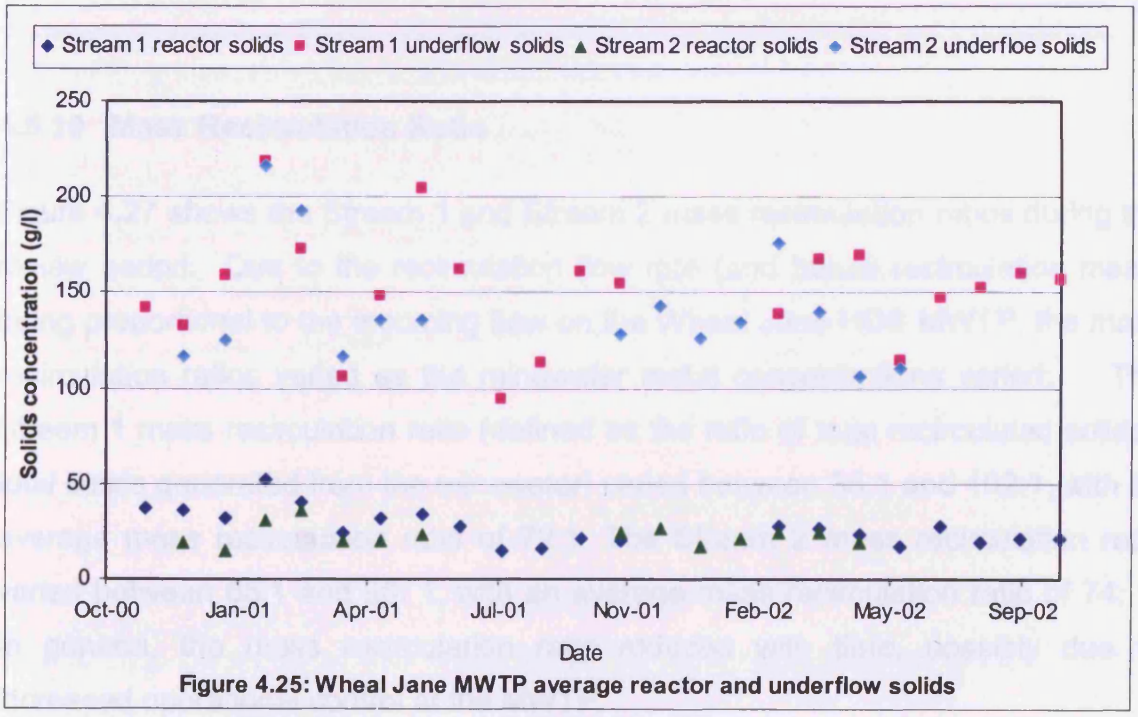


Figure 4.25: Wheal Jane MWTP average reactor and underflow solids

The reactor solids concentrations averaged 27 g/l and 23 g/l for Stream 1 and Stream 2 respectively, and the clarifier underflow solids concentration averaged 151 g/l and 140 g/l for Stream 1 and Stream 2 respectively.

4.5.9 Volumetric Recirculation Ratio

The variations of the volumetric recirculation ratio throughout the review period are shown in Figure 4.26. The average Stream 1 and Stream 2 volumetric recirculation ratios were 0.21 m^3 of recirculation flow per m^3 of minewater.

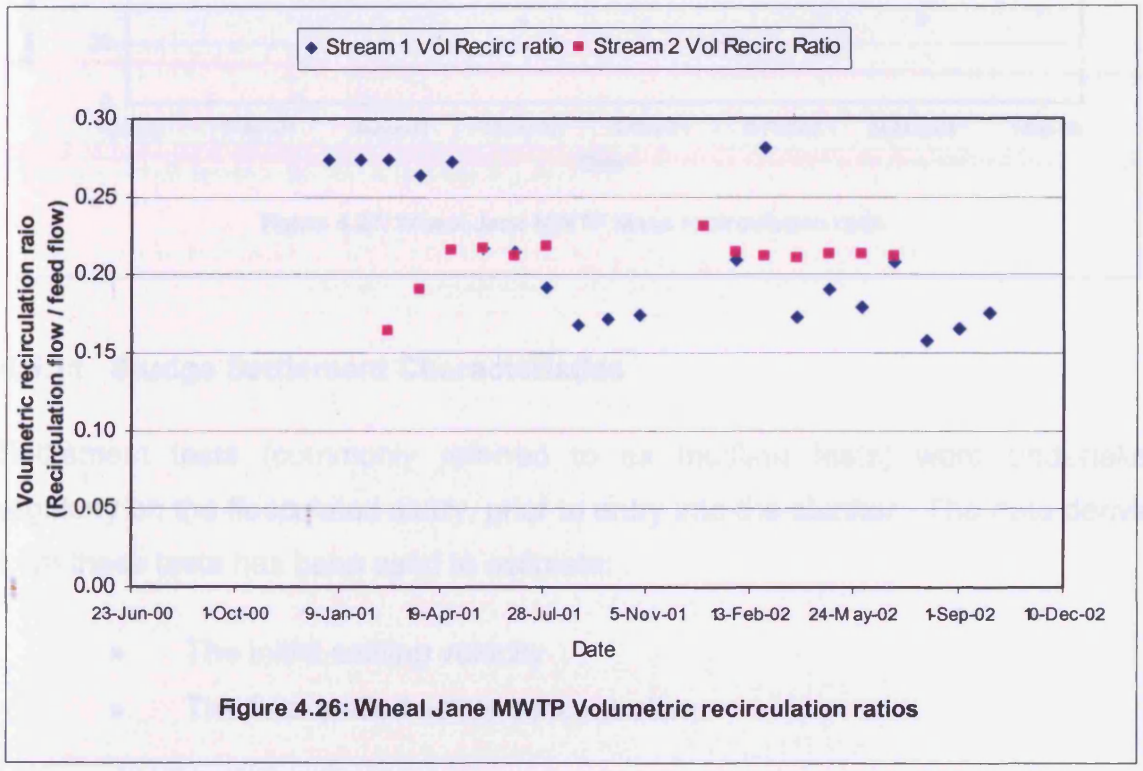


Figure 4.26: Wheal Jane MWTP Volumetric recirculation ratios

4.5.10 Mass Recirculation Ratio

Figure 4.27 shows the Stream 1 and Stream 2 mass recirculation ratios during the review period. Due to the recirculation flow rate (and hence recirculation mass) being proportional to the incoming flow on the Wheal Jane HDS MWTP, the mass recirculation ratios varied as the minewater metal concentrations varied. The Stream 1 mass recirculation ratio (defined as the ratio of total recirculated solids / total solids generated from the minewater) varied between 36:1 and 102:1, with an average mass recirculation ratio of 72:1. The Stream 2 mass recirculation ratio varied between 65:1 and 96: 1, with an average mass recirculation ratio of 74: 1. In general, the mass recirculation ratio reduced with time, possibly due to increased operational control at the MWTP.

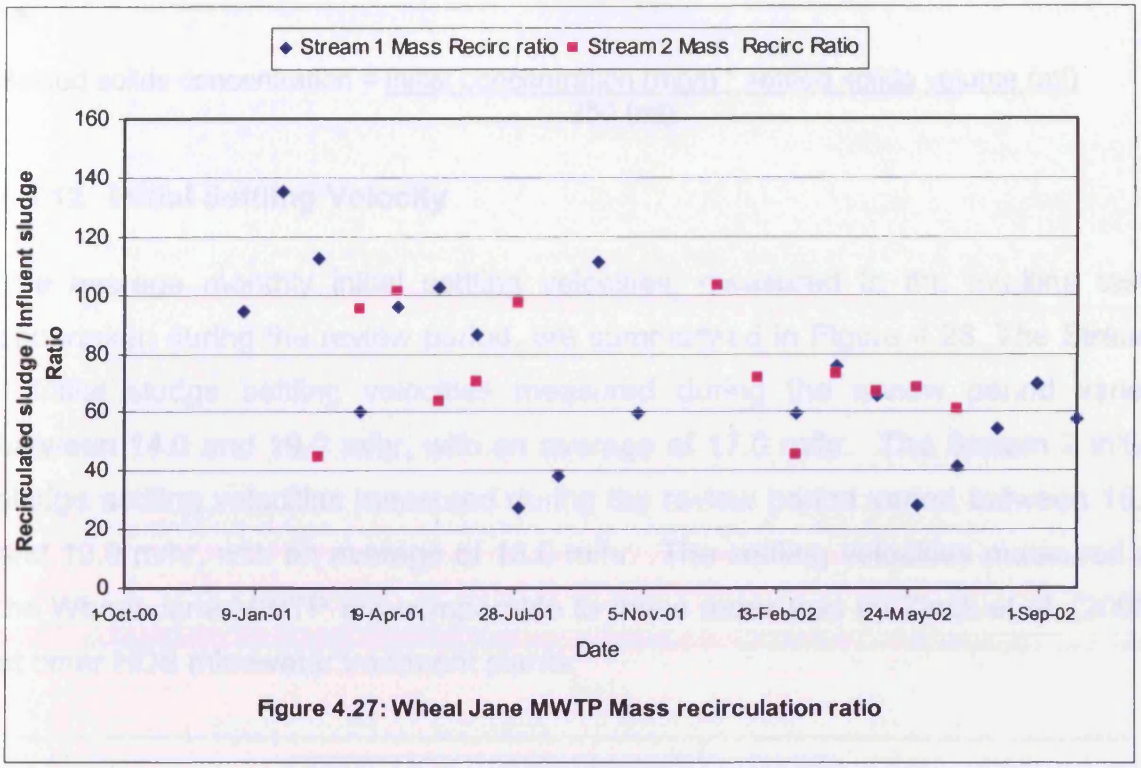


Figure 4.27: Wheal Jane MWTP Mass recirculation ratio

4.5.11 Sludge Settlement Characteristics

Settlement tests (commonly referred to as mudline tests) were undertaken regularly on the flocculated slurry, prior to entry into the clarifier. The data derived from these tests has been used to estimate:

- The initial settling velocity
- The final settled solids concentration.

The settling velocity of the solids in the wastewater was determined by measuring the height of the interface between the solids and the clear supernatant water in a 250ml measuring cylinder at time 0, 0.5,1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 60 and 120 minutes during the mudline test. The initial settlement velocity was calculated by dividing the distance the interface had dropped in the first 0.5 minutes by 0.5 minutes. The unit conventionally used for initial settling velocity is m/hr.

i.e.

$$\text{Initial settling velocity} = \frac{\text{distance interface dropped in 0.5 min (m)}}{0.033\ (\text{hr})}$$

The volume occupied by the solids after 120 minutes was used to calculate the settled solids concentration.

i.e.

$$\text{Settled solids concentration} = \frac{\text{initial concentration (mg/l)} * \text{settled solids volume (ml)}}{250\ \text{(ml)}}$$

4.5.12 Initial Settling Velocity

The average monthly initial settling velocities, measured in the mudline tests undertaken during the review period, are summarised in Figure 4.28. The Stream 1 initial sludge settling velocities measured during the review period varied between 14.0 and 19.0 m/hr, with an average of 17.0 m/hr. The Stream 2 initial sludge settling velocities measured during the review period varied between 16.0 and 19.0 m/hr, with an average of 18.0 m/hr. The settling velocities measured at the Wheal Jane MWTP are comparable to those measured by Zinck et al. (2001) at other HDS minewater treatment plants.

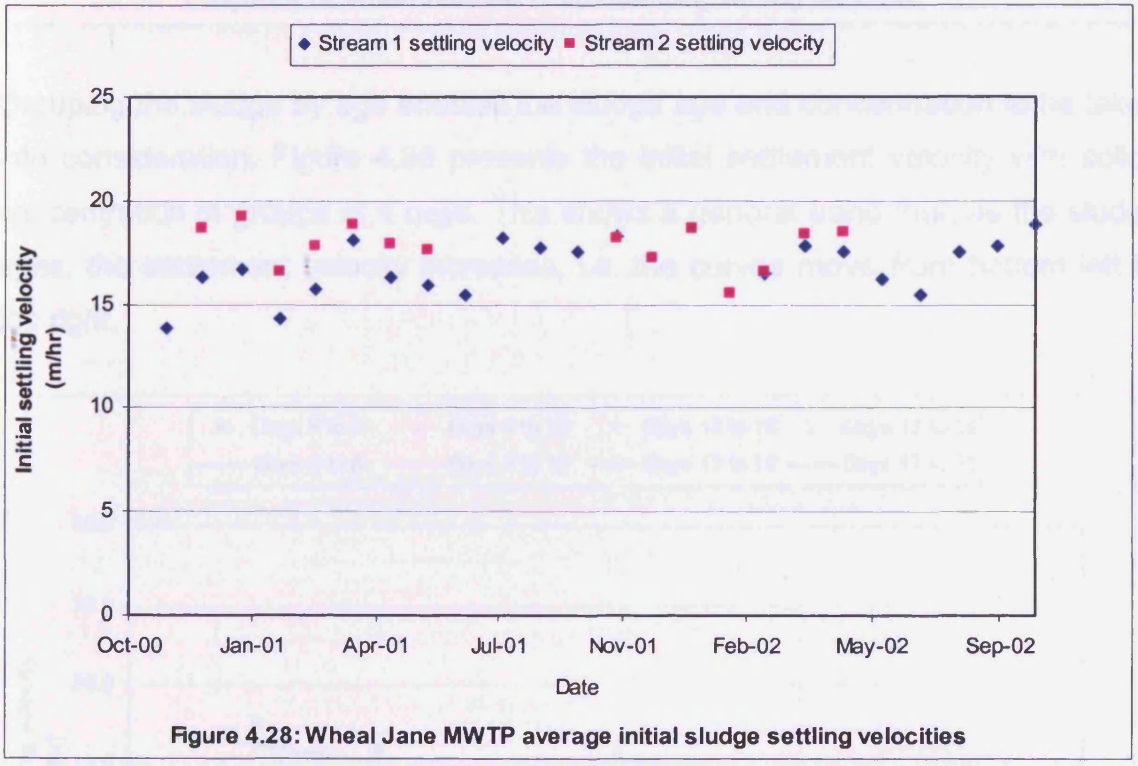


Figure 4.28: Wheal Jane MWTP average initial sludge settling velocities

The initial settling velocities measured in the mudline tests during the first two weeks of commissioning are summarised in Figure 4.29. This indicates an average commissioning settling velocity of 14.8 m/hr.

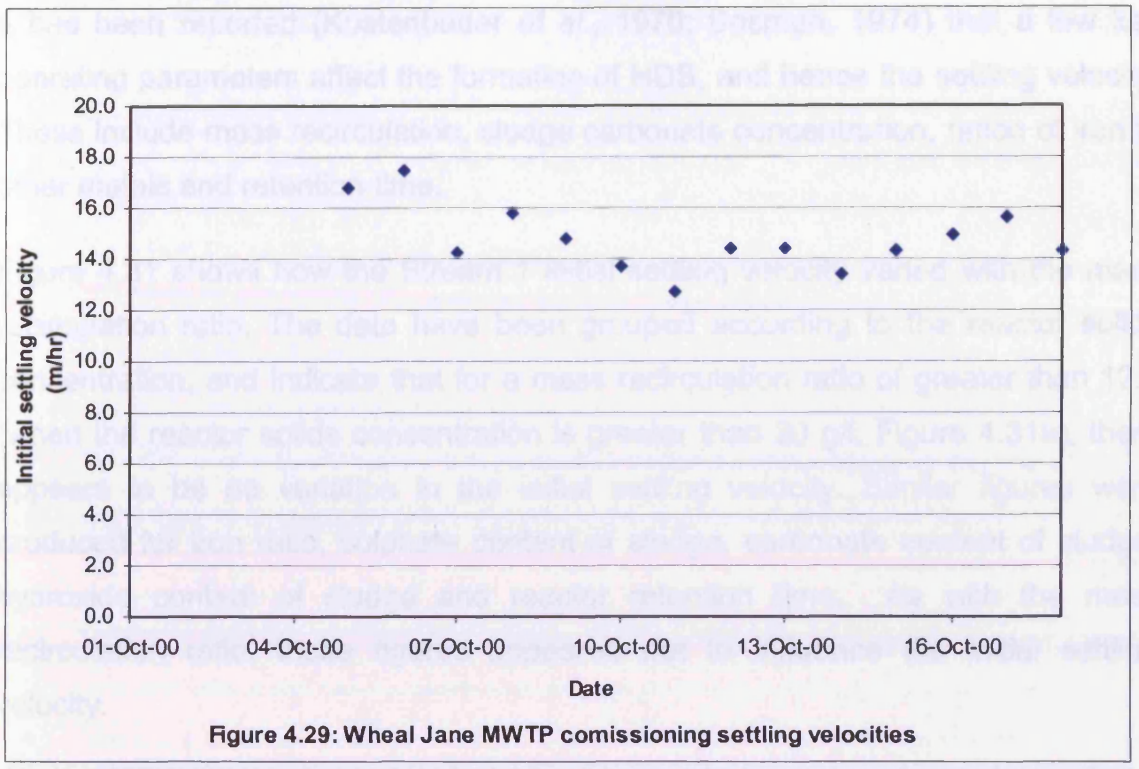


Figure 4.29: Wheal Jane MWTP comissioning settling velocities

Grouping the sludge by age enables the sludge age and concentration to be taken into consideration. Figure 4.30 presents the initial settlement velocity with solids concentration in groups of 4 days. This shows a general trend that, as the sludge ages, the settlement velocity increases, i.e. the curves move from bottom left to top right.

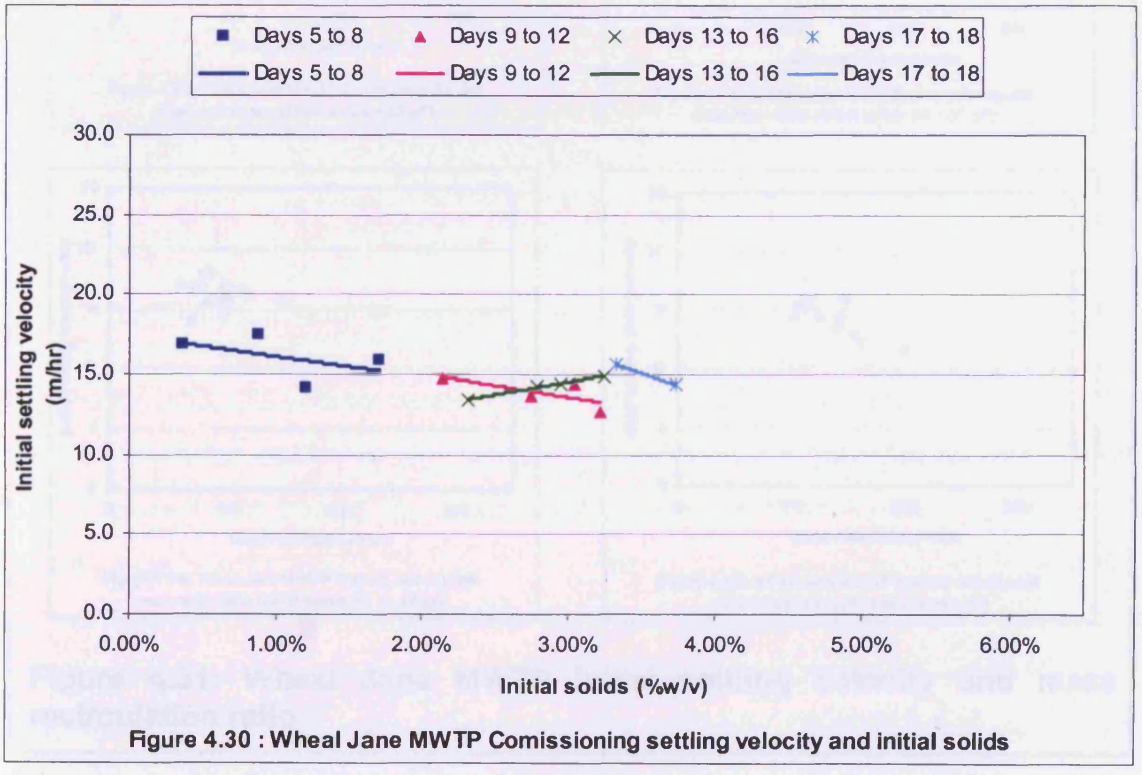


Figure 4.30 : Wheal Jane MWTP Comissioning settling velocity and initial solids

It has been reported (Kostenbader *et al.*, 1970; Bosman, 1974) that a few key operating parameters affect the formation of HDS, and hence the settling velocity. These include mass recirculation, sludge carbonate concentration, ration of iron to other metals and retention time.

Figure 4.31 shows how the Stream 1 initial settling velocity varied with the mass recirculation ratio. The data have been grouped according to the reactor solids concentration, and indicate that for a mass recirculation ratio of greater than 12.3 (when the reactor solids concentration is greater than 20 g/l, Figure 4.31a), there appears to be no variation in the initial settling velocity. Similar figures were produced for iron ratio, sulphate content of sludge, carbonate content of sludge, hydroxide content of sludge and reactor retention time. As with the mass recirculation ratio, these figures appeared not to influence the initial settling velocity.

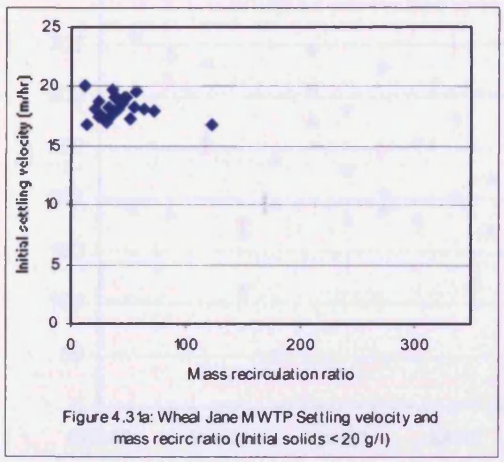


Figure 4.31a: Wheal Jane MWTP Settling velocity and mass recirc ratio (Initial solids < 20 g/l)

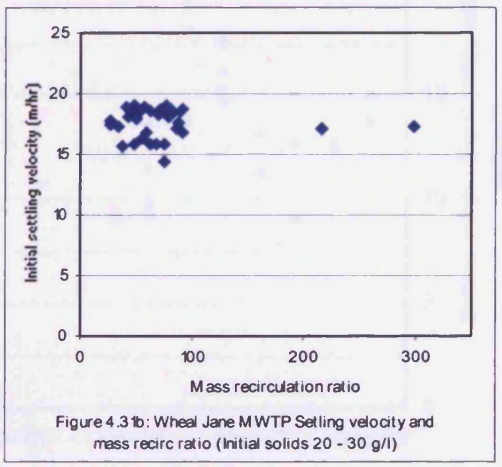


Figure 4.31b: Wheal Jane MWTP Setling velocity and mass recirc ratio (Initial solids 20 - 30 g/l)

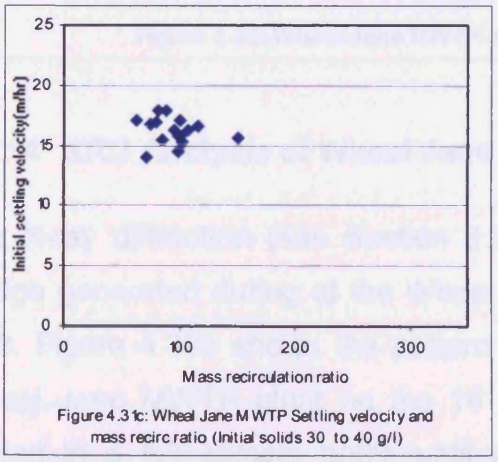


Figure 4.31c: Wheal Jane MWTP Settling velocity and mass recirc ratio (Initial solids 30 to 40 g/l)

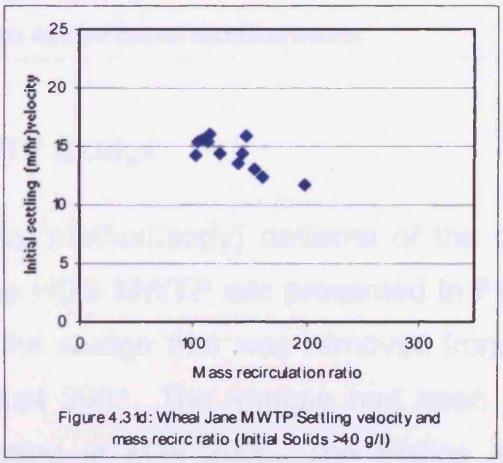


Figure 4.31d: Wheal Jane MWTP Settling velocity and mass recirc ratio (Initial Solids >40 g/l)

Figure 4.31: Wheal Jane MWTP Initial settling velocity and mass recirculation ratio

4.5.13 Settled Solids Content

The variation in the settled mudline solid concentrations after 2 hours is shown in Figure 4.32. The Stream 1 settled solids concentration averaged 309 g/l, whilst Stream 2 averaged 288 g/l.

Figure 4.32 also presents the ratio of settled (post settlement) solids to initial (pre settlement) solids, with average ratios of approximately 11.9 for Stream 1 and 13.0 for Stream 2, which indicate a sludge of good settling characteristics. This is an important ratio as this indicates how well the sludge will compact during settlement and hence how the volume of the sludge to be removed will be reduced.

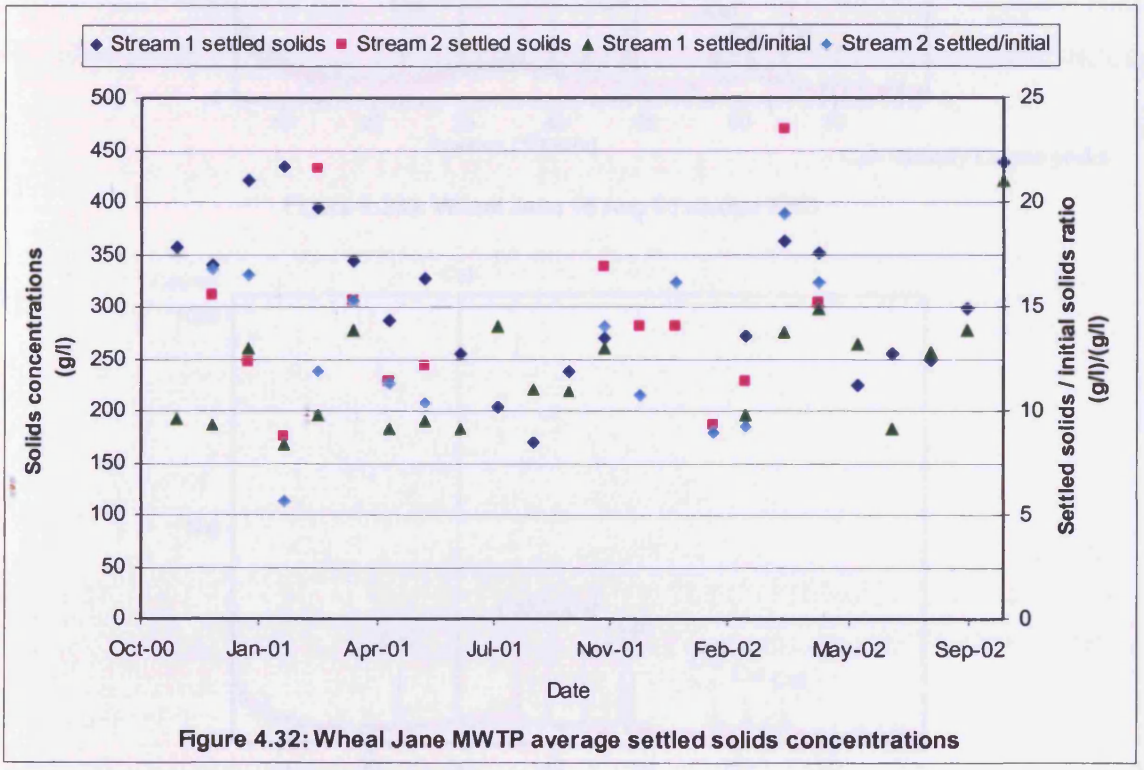


Figure 4.32: Wheal Jane MWTP average settled solids concentrations

4.5.14 XRD Analysis of Wheal Jane MWTP Sludge

The X-ray diffraction (see Section 3.3.1 for methodology) patterns of the dried sludge generated during at the Wheal Jane HDS MWTP are presented in Figure 4.33. Figure 4.33a shows the pattern for the sludge that was removed from the Wheal Jane MWTP plant on the 16 August 2001. The sample had been kept sealed in a full sample bottle until analysed in May 2005. The Philips Xpert Industry software indicated that the only mineral present was Calcite ($CaCO_3$), no crystalline iron minerals were detected by the software. As with the sludge sample removed on the 16 August 2001, the sludge removed from the plant on the 10

February 2005 was shown only to have calcite minerals present. With both sludge samples, the presence of the calcite peaks may have masked other peaks present.

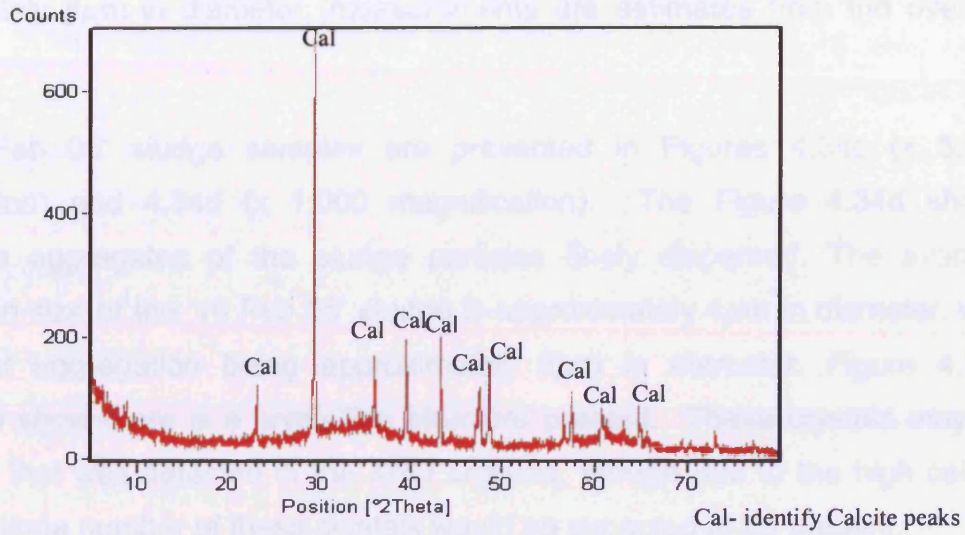


Figure 4.33a: Wheal Jane 16 Aug 01 sludge XRD

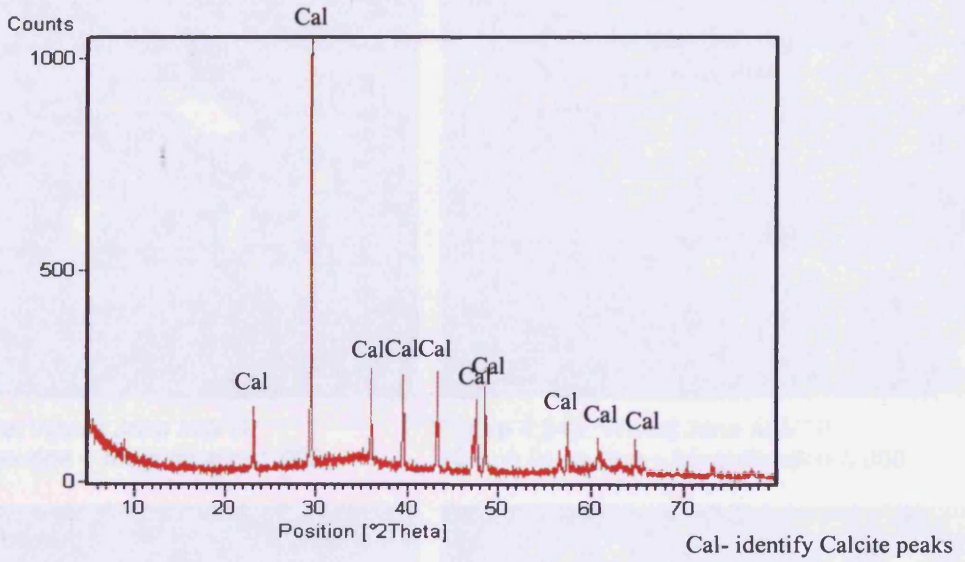


Figure 4.33a: Wheal Jane 10 Feb 05 sludge XRD

Figure 4.33: Wheal Jane MWTP sludge XRD traces

4.5.15 SEM Analysis

The results of the SEM analysis of Wheal Jane MWTP sludge are presented in Figure 4.34 (see Section 3.4.3 for methodology). The analysis of the '16 Aug 01' sludge sample is presented in Figures 4.34a (x 5,000 magnification) and 4.34b (x 1,000 magnification). Figure 4.34b (which is slightly blurred due to the image capture methodology) shows amorphous aggregates of the sludge particles finely

dispersed. Figure 4.34a appears to show the edges of the sludge to be very 'soft' in nature. Figure 4.34a also shows that the sludge particles appear to be 'welded' together in one gelatinous form. The average aggregation size of the '10 Feb 05' sludge is approximately 4μm in diameter, with the largest aggregation being approximately 8μm in diameter (measurements are estimates from the overlaid scale).

The '10 Feb 05' sludge samples are presented in Figures 4.34c (x 5,000 magnification) and 4.34d (x 1,000 magnification). The Figure 4.34d shows amorphous aggregates of the sludge particles finely dispersed. The average aggregation size of the '10 Feb 05' sludge is approximately 4μm in diameter, with the largest aggregation being approximately 8μm in diameter. Figure 4.34c appears to show there is a crystalline structure present. These crystals may be the calcite that was detected in the XRD analysis, though due to the high calcite content, a large number of these crystals would be expected to be present.

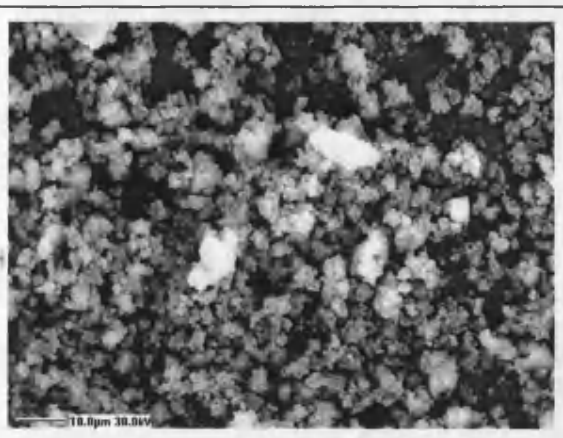


Figure 4.34a: Wheal Jane MWTP
16 Aug 01 sludge – Magnification1,000

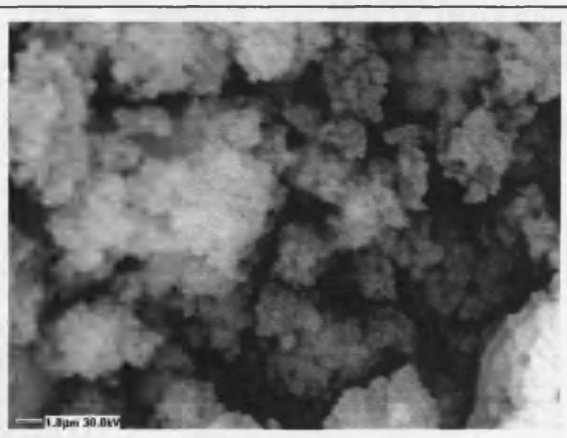


Figure 4.34b: Wheal Jane MWTP
16 Aug 01 sludge – Magnification 5,000

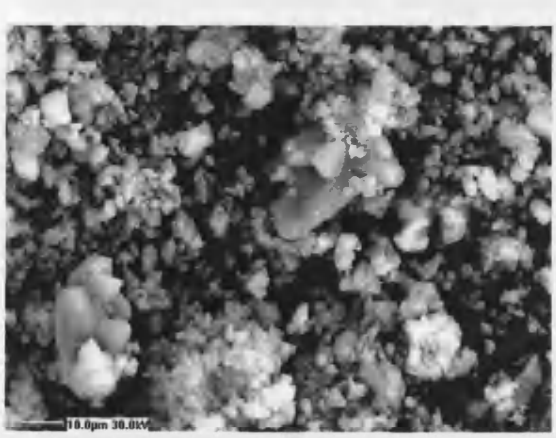


Figure 4.34c: Wheal Jane MWTP
10 Feb 05 sludge – Magnification1,000

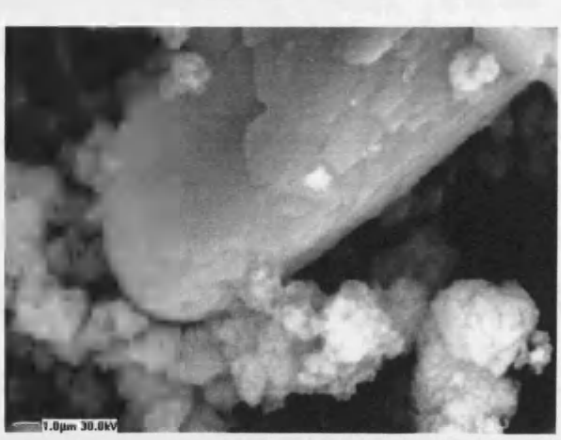


Figure 4.34d: Wheal Jane MWTP
10 Feb 05 sludge – Magnification 5,000

Figure 4.34: Wheal Jane MWTP SEM micrographs

4.5.16 Sludge Disposal

During the review period, a total of approximately 9.2 x 10^3 tonnes of dried solids were removed from the minewater. This was pumped to the CVTD in 140 x 10^3 m^3 of slurry at a concentration of 65.8 g/l. The difference between the clarifier underflow concentrations (average of 147 g/l) and the sludge to the CVTD concentrations (average of 65.8 g/l) is likely to have been caused by the sludge line flushing water. It is estimated that approximately 59% (5.4 x 10^3 tonnes) of the solids were metal hydroxides, with the remainder being 'other elements', including calcium carbonate, inert material and un-reacted lime slurry.

4.5.17 Power Used

During the period 1st October 2000 and 31st July 2002, a total of 7.6 x 10^6 kWhr of electricity was used pumping and treating the Wheal Jane minewater. Pumping the minewater out of the ground accounted for 3.6 x 10^6 kWhr (47%), whilst running the MWTP used 4.0 x 10^6 kWhr (53%). Therefore, the MWTP (excluding pumping) used 0.33 kW/m^3 of minewater treated. Alternatively, the consumption can be expressed as 0.44 kW/kg of solids removed from the Wheal Jane minewater.

4.5.18 Wheal Jane MWTP Economics

The principal economics of the Wheal Jane MWTP are shown in Table 4.7.

Table 4.7: Wheal Jane MWTP Project Economics

Total budget for consultancy, design, build and 10 year operating contract	£16.9M
Target costs for the construction of the Phase I plant	£3.9M
Actual cost of the Phase I plant	£3.4M
Actual cost of Phase II works	£0.3M
Saving on Phase II works	£1.7M
Annual operating cost	£1.0M
Predicted operating cost (predicted to vary with declining concentration)	£0.16 to £0.20/m^3
Predicted average operating cost for the 10 year contract period	£0.17/m^3
Actual operating cost over first 2 years per m^3 of water treated	£0.18/m^3
Actual operating cost over the first 2 years per kg of metal removed	£0.64/kg

Note: the operating costs include contactor management fee, profit, fixed costs (including sludge disposal) and variable costs (including pumping of the minewater).

The predicted average operating cost at 17p/m^3 was based on the average metal concentration projected for the 10 year operating contract, taking into account the ongoing decline in metal concentrations. Consequently, treatment costs were anticipated to decrease throughout the contract period as the metal concentration declined to between 20p/m^3 and 16p/m^3, as shown in Table 4.7. The actual average operating cost achieved over the first two years (18p/m^3) is comparable with the predicted long-term average, and therefore represents a reduction in the anticipated unit cost for this period.

4.5.19 Summary of Wheal Jane MWTP Operational Review

The key performance parameters of the Wheal Jane MWTP are presented in Table 4.8, with general comments listed below.

Stream 1 Stage 1 reactor pH stabilised at 8.0, when the solids concentration reached 20.0 g/l (Figure 4.19).

The ratio of settled solids to initial solids was 11.9 for Stream 1 and 13.0 for Stream 2.

The average clarifier feed sludge initial settling velocity was 17 m/hr in Stream 1 and 18 m/hr in Stream 2. It appeared that, once a minimum mass recirculation ratio was reached, the settlement velocity did not increase. It was also noticed that carbonate and sulphate composition of the solids, retention time and iron content (as a ratio to other metals concentrations in the minewater) did not affect the settlement velocity.

Table 4.8: Wheal Jane MWTP key performance parameters

	MWTP Average	Stream 1 Average	Stream 2 Average
Flow rates			
Average feed flow rate (m^3/day)	17,200		
Average recirculation flow rate (m^3/day)	2,390		
Feed Metals (mg/l)			
Calculated average total mixed metal concentration	262		
Average Zn	44.4		
Average Fe	191		
Average Mn	5.8		
Average Al	20.0		
Average Cu	7.4		
Retention Time (min)			
Stage I/ Stage II		61	75
pH (pH units)			
Influent	2.2		
Stage I		7.84	8.63
Stage II		9.25	9.25
Effluent	8.7		
Redox (mV)			
Influent	245		
Stage I	207		
Stage II	178		
Effluent	215		
Reagent Use			
Calcium hydroxide consumption (g of calcium hydroxide / g of metal)	2.40		
Calcium hydroxide consumption (mg of calcium hydroxide /l of minewater)	0.60		
Calcium hydroxide efficiency (%)	69.8		
Flocculant dose (mg/l)	2.13		
Sludge Generation Rate (mg/l)		762	720
Volumetric Recirculation Ratio		0.21	0.21
Mass Recirculation Ratio		72	74
Sludge Characteristics			
Reactor Solids (g/l)		27	23
2 Hour Settled Solids (g/l)		309	288
Recycle solids (g/l)		151	140
Initial settling Velocity (m/hr)		17	18
Settled/ Initial solids ratio		11.9	13.0

5 LABORATORY STUDIES – BATCH TESTS

5.1 Introduction to Batch Tests

Chapter 2 outlined the common processes used in the high density sludge process for treating acidic minewaters. The key parameters associated with the formation have been hypothesised by Kostenbader *et al.* (1970) and Bosman (1974), Section 2.13.

To examine the importance of the parameters it was decided in the present study to undertake a series of laboratory experiments. Ideally a continuous process treating fresh minewater would be used (Bosman, 1980, Dey M *et al.*, 2004) to test out the importance of these parameters. As continuous trials are not always possible, laboratory batch tests offer an alternative for establishing suitability of the HDS process on an individual waste stream (Bosman, 1980, Dey M *et al.*, 2004 and Coulton *et al.*, 2004c).

It was proposed to undertake a series of laboratory batch tests to carry out initial screening tests on synthetic minewater with different base metals using different alkali reagents. The objectives of the tests were to:

1. Generate HDS sludge using Type II HDS process by undertaking batch tests on synthetic minewater, enabling a comparison with the results from Wheal Jane MWTP to be undertaken.
2. Show that Type II HDS sludge could be formed using various alkali reagents.
3. Demonstrate that Type II HDS could be formed by non-or low iron feed water (as with Britannia (Canada) minewater (Section 2.2)), and hence check the importance of iron.
4. Investigate the effect of seawater on the formation of Type II HDS.

As shown in Chapters 3 and 4, high density sludge can be formed on the Wheal Jane minewater using the Unipure HDS process with calcium hydroxide as the neutralising reagent. It was therefore decided the batch tests would be based around this process. Synthetic Wheal Jane minewater was produced and calcium hydroxide used as the initial alkali reagent. Subsequently sodium hydroxide, magnesium hydroxide and sodium carbonate were used as the alkali reagents. A

further series of tests was performed using zinc and aluminium in solution. Finally, a series of tests were undertaken using synthetic minewater made from iron in seawater. A summary of the batch tests undertaken is presented in Table 5.1.

Table 5.1: Summary of batch tests

Test No	Description	Synthetic Minewater Composition		Final pH
		Determinand	mg/l	
1	Synthetic Wheal Jane minewater treated with calcium hydroxide	pH Iron Zinc Copper Manganese Aluminium	3.5 (pH units) 237 45.7 0.1 6.5 20.0	9.2
2	Synthetic Wheal Jane minewater treated with sodium hydroxide	pH Iron Zinc Copper Manganese Aluminium	3.5 (pH units) 237 45.7 0.1 6.5 20.0	9.2
3	Synthetic Wheal Jane minewater treated with magnesium hydroxide	pH Iron Zinc Copper Manganese Aluminium	3.5 (pH units) 237 45.7 0.1 6.5 20.0	9.2
4	Synthetic Wheal Jane minewater treated with sodium carbonate	pH Iron Zinc Copper Manganese Aluminium	3.5(pH units) 237 45.7 0.1 6.5 20.0	9.2
5	Synthetic zinc minewater treated with calcium hydroxide	pH Zinc	3.5 (pH units) 200	9.2
6	Synthetic aluminium minewater treated with calcium hydroxide	pH Aluminium	3.5 (pH units) 200	9.2
7	Synthetic iron in seawater minewater treated with calcium hydroxide	pH Iron Seawater	6.0 (pH units) 200	8.5
8	Synthetic iron in seawater minewater treated with sodium hydroxide	pH Iron Seawater	6.0 (pH units) 200	8.5
9	Synthetic iron in seawater minewater treated with sodium carbonate	pH Iron Seawater	6.0 (pH units) 200	8.5

5.2 Batch Test Methodology

5.2.1 Bosman Methodology for Using Batch-type Laboratory Tests

The Bosman (1980) methodology for simulating the high density sludge process in the laboratory on a batch basis is conducted as follows:

1 Neutralise a 500 ml portion of acid water to pH 7.2 – 7.4 with a known

quantity of lime in slurry form while agitating with compressed air. Continue the aeration for a further 10 minutes to ensure oxidation of the Fe (II).

2 Pour into a 1-litre measuring cylinder and allow sludge to settle for one hour.

3 Record the volume of settled sludge and decant or siphon off the supernatant water.

4 Transfer the sludge to a beaker and add the same quantity of lime as in step 1 while stirring slowly. Continue stirring for 20 minutes.

5 Add the conditioned sludge/lime mixture to another 500 ml portion of acid water as in step 1 and repeat the procedures until a graph as in Figure 5.1 flattens off.

Adjustments in the quantity of lime added to subsequent portions may be necessary if the neutralized water deviates from the recommended value.

If no HDS is found, a straight line such as Line A in Figure 5.1 (Bosman 1980) will be obtained. If HDS is formed, a curve similar to B should be obtained. The number of cycles at point C, when the volume of the sludge produced reaches its maximum, on graph B, can be used as an indication of the recycle ratio required in a continuous plant.

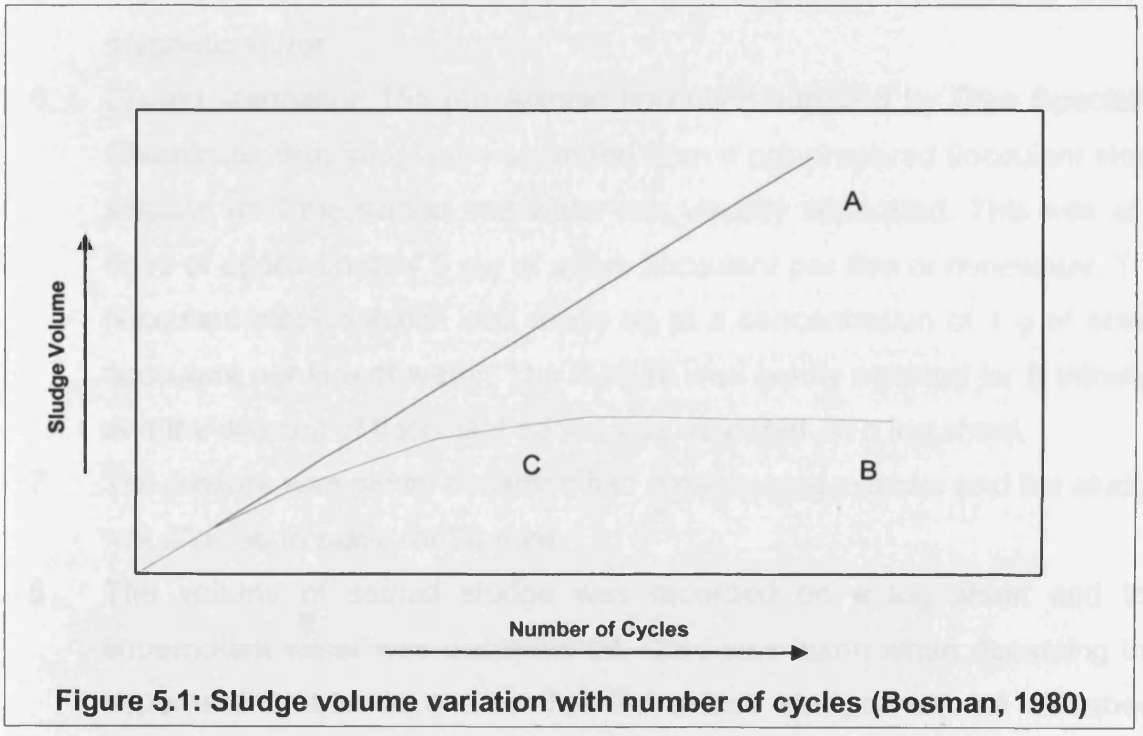


Figure 5.1: Sludge volume variation with number of cycles (Bosman, 1980)

The above methodology is to test the Type I HDS process (see Section 2.8) where sludge conditioning occurs prior to neutralisation of a given minewater, i.e. the Tetra style HDS process (Bosman, 1980).

Using this principle, a modified methodology was produced to simulate the Type II HDS process (see Section 2.8) being used at Wheal Jane MWTP.

5.2.2 Methodology for Using Batch-type Laboratory Tests on the Type II HDS Process

The simulation of the Type II HDS process in the laboratory on a batch basis was conducted as follows:

1 1 litre of acid minewater was added to a 1.5 litre reactor vessel.

2 The minewater was gently agitated with a mixer (Wemco and Denver Flotation unit, see Section 5.4) for 30 mins.

3 Alkali reagent was added to the minewater to ensure the desired pH (Table 5.1) is reached. The minewater was vigorously agitated with a mixer and compressed air added, at a rate of 2.7 litre/hr. The amount of alkali reagent added was recorded on a log sheet.

4 The process was continued for a total of 30 minutes to ensure oxidation of the Fe (II), if present.

5 The contents were transferred to a beaker and gently agitated with a magnetic stirrer.

6 Diluted Magnafloc 155 (an Anionic flocculant supplied by Ciba Specialist Chemicals, Bradford, UK) was added from a pre-prepared flocculant stock solution until the sludge and water mix visually separated. This was at a dose of approximately 5 mg of active flocculant per litre of minewater. The flocculant stock solution was made up at a concentration of 1 g of active flocculant per litre of water. The mixture was gently agitated for 5 minutes and the amount of flocculant added was recorded on a log sheet.

7 The mixture was gently decanted into a measuring cylinder and the sludge mix allowed to settle for 30 mins.

8 The volume of settled sludge was recorded on a log sheet and the supernatant water was decanted off. Care was taken when decanting the supernatant water to ensure that the settled sludge was not disturbed. Samples of the supernatant and the settled sludge were taken after every

fifth cycle, see Step 9.

9 The settled sludge was transferred back to the 1.5 litre reactor vessel and a further 1 litre of fresh minewater added and steps 2 – 8 were repeated.

10 The batch test was repeated 25 times or until a curve similar to graph B in Figure 5.1 was obtained.

5.2.3 Additional Analysis/Recordings Required

The primary aim of the batch tests was to note the effect of the different alkali reagent on the volume of the generated sludge after 30 minutes settlement time. To further help the understanding of the parameters involved in the generation of HDS sludge, the following items were recorded during the batch tests.

1 Initial metal concentrations, i.e. Total Fe, Total Al, Total Mn and Total Zn.

2 Supernatant water quality, i.e. the decanted clean water was analysed every 5 cycles for solids concentration. The final supernatant Total Fe, Total Al, Total Mn, Total Zn, Total 'Hydroxide' and Total CO_3 concentrations were also measured.

3 Settled sludge was sampled, 40ml every fifth cycle, and analysed for solids concentration, Total Fe, Total Zn, Total Al, Total Mn, Total Ca, Total CO_3 and Total 'Hydroxide' concentrations. These were used to indicate how the sludge changed form. SEM analysis was also undertaken on the sludge to compare the morphology of the sludge generated during the batch tests.

4 pH and Redox were recorded.

5.3 Synthetic Minewater Quality

A total of four tests were undertaken on synthetic Wheal Jane minewater using four different alkali reagents; calcium hydroxide, sodium hydroxide, magnesium hydroxide and sodium carbonate. Hypothetical synthetic zinc minewater and aluminium minewater were dosed with calcium hydroxide, which were used as a means of checking the importance of iron in the formation of HDS. The final synthetic minewater, iron in seawater with added calcium, was treated with calcium hydroxide, sodium hydroxide and sodium carbonate. During the seawater batch tests the seawater was collected from Sully Head, a point in the Severn Estuary, south west of Cardiff. The seawater batch tests were undertaken as there are a number of locations in the United Kingdom, e.g. Horden MWTP in County

Durham (Coulton *et al.* 2004), where abandoned coal mines have highly saline water.

The iron was added as Fe (II) chloride, zinc as zinc chloride, aluminium as aluminium sulphate and manganese as manganese chloride by adding dry powders, supplied by Fisher Chemicals, to 50 l of deionised water during Batch test 1 to 4 and tap water during Batch Tests 5 to 9. The pH was adjusted to ensure all metals remained in solution. The minewater quality was analysed during each batch test.

5.4 Alkali Reagents Used

The alkali reagents (see Section 1.0) used during the batch tests were calcium hydroxide (at a concentration of 22.9 g/l), magnesium hydroxide (at a concentration of 286 g/l), sodium hydroxide (at a concentration of 20.0 g/l) and sodium carbonate (at a concentration of 53.0 g/l). The concentrations of calcium hydroxide, sodium hydroxide and sodium carbonate were chosen to ensure the volumes of the alkali reagent added were no greater than 5% of the minewater volume. The magnesium hydroxide used was 'Magmex', a commercial magnesium hydroxide product, supplied by Omex Environmental, Kings Lynn, Norfolk, UK.

5.5 Equipment Description

Two laboratory flotation cells were used during the batch tests, enabling twice as many tests to be undertaken These were a Wemco flotation cell (Figure 5.2a), manufactured by Western Machining Company of California, and a Denver flotation cell (Figure 5.2b) operated at 1250 rpm. Due to the different rotors (Figure 5.2c and Figure 5.3d) the Wemco cell exerted more shearing energy and input more air into the cell contents. Batch Tests 1, 2, 3 and 4 were undertaken on both flotation cells, Batch Test 5 was undertaken on the Wemco flotation cell, Batch Test 6 was undertaken on the Denver flotation cell and Batch Tests 7, 8 and 9.

Due to the design of the Wemco unit, i.e. rotor design and aeration system, more air was introduced by the Wemco flotation cell compared to the Denver flotation cell. This potentially increased oxidation rates and the rate at which carbon dioxide was introduced to the system and hence the rate of carbonate production (Section 5.6.2).

Figure 5.2a: Denver flotation cell

Figure 5.2b: Wemco flotation cell

Figure 5.2c: Denver rotor

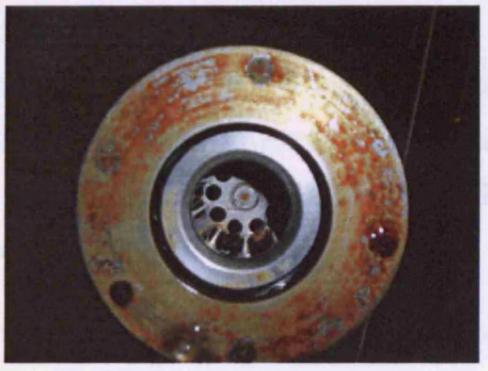


Figure 5.2d: Wemco rotor

Figure 5.2: Batch test Denver and Wemco flotation cells

5.6 Batch Test 1 – Synthetic Wheal Jane Minewater treated with Calcium Hydroxide

As outlined in Section 5.1, Batch Test 1 involved dosing synthetic Wheal Jane minewater with calcium hydroxide, as used on the full scale MWTP at Wheal Jane. This batch test was used to confirm that Type II HDS can be produced by this method and the results generated would be used as a control to compare other test results.

During the test 50 litres of synthetic Wheal Jane minewater was made up. The metals were added, introduced as metal chloride or sulphate powders (Section 5.3) supplied by Fisher Chemicals, directly to 50 litres of deionised water with sulphuric acid added to correct the pH. The pH correction also ensured the metals

remained in solution. The desired Wheal Jane minewater is presented in Table 5.2, as is the actual feed water used in Batch Test 1.

Table 5.2: Batch Test 1 Water Quality Summary

Sample	pH	Suspended Solids mg/l	Total Fe mg/l	SO_4 mg/l	Ca mg/l	Zn mg/l	Mn Mg/l	Al mg/l
Wheal Jane minewater	3.5	5	200	500	100	45	6	20
Batch Test 1 Feed water	2.0	166	199	216	<1	63	8	25
Treated water	5.3	49	24	486	217	4.4	-	2.4

Due to the results not being analysed fully until after the batch test was completed, it is unsure why the total suspended solids were so high in the synthetic minewater. The iron, zinc, manganese and aluminium concentrations compared well with the Wheal Jane minewater, though the calcium concentration was much lower than the Wheal Jane minewater, due to deionised water being used to make the synthetic minewater, and as the iron, zinc and aluminium were added as chloride compounds, the sulphate concentrations were lower than the Wheal Jane minewater. However, as the object was to compare the formation of HDS sludge, this was not considered to be of significant importance.

For Batch Test 1, a total of 35 cycles were undertaken with the feed water and treated water quality as presented in Table 5.2. The desired treated water quality for each individual metal residual concentration was less than 1 mg/l. The pH of the treated water sample analysed was 5.3, resulting in higher than anticipated treated water residual metal concentrations. It is considered that these results are not indicative of the water quality during the whole of the test.

5.6.1 Batch Test 1 – Sludge Volume and Mass of Solids

As described by Bosman (1983), the volume occupied by the treated sludge can be used as an indication of whether HDS has been formed. Presented in Figure 5.3 is how the measured sludge volume and the measured sludge mass in the system vary with the number of cycles for the Wemco flotation cell. The measured sludge mass is a product of the sludge concentration and the measured sludge volume. The sludge concentrations are also presented in Table 5.3 along with the supernatant and initial solids concentrations.

As the number of cycles increases, the sludge volume first increases then

decreases to a minimum after 30 cycles. However, if the sludge mass had also decreased (due to sampling errors and not all the solids being transferred when the fluids were moved from one vessel to another), this would explain why the volume had decreased. Therefore, a mass balance was undertaken on the sludge generated during the batch test, see below. Figure 5.3 shows how the measured sludge mass increases from circa 2.5 g after cycle 5 (when the measured sludge volume was approximately 150 ml) to 8.0 g after cycle 35, when the measured sludge volume had decreased by 57% to approximately 65 ml. As the graphs presented in Figure 5.4 were similar to the graph presented in Figure 5.1 only 35 cycles were undertaken..

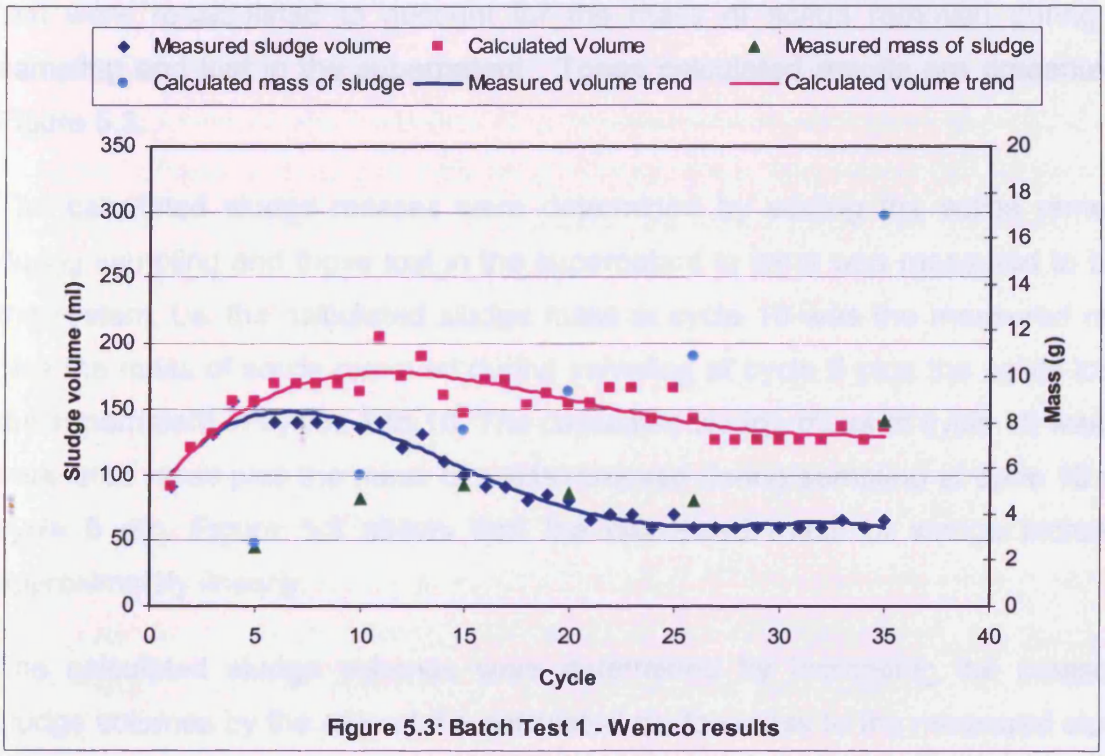


Figure 5.3: Batch Test 1 - Wemco results

Table 5.3: Batch Test 1 Wemco sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 20	Cycle 26	Cycle 35
Initial solids	g/l	2.2	4.1	4.7	4.5	4.3	7.6
Sludge solids	g/l	16.5	34.8	52.4	61.2	76.3	124
Supernatant solids	mg/l	25	84	119	144	43	86

The final measured sludge mass was 8.07 g of dried solids. However, due to the solids removed from the system during sampling, and solids lost in the supernatant water, this is an underestimation of the total solids generated during

the batch test. During Batch Test 1, a total of 6.03 g of dried solids was removed for analysis prior to the final sludge volume reading. The solids lost from the system in the supernatant water were calculated as a product of the supernatant solids concentration and the volume of supernatant removed per cycle. During the Wemco Batch Test 1, this totalled 2.89 g. This would indicate that the total mass of solids generated during the batch test was 17.0 g of dried solids or a solids generation rate of 485 mg of solids per litre of minewater treated.

The removed sludge mass of 6.03 g of dried solids, and solids lost in the supernatant of 2.89 g of dried solids represented approximately 52.5 % of the total solids generated. Therefore, the sludge volumes and sludge masses for the batch test were recalculated to account for the mass of solids removed during the sampling and lost in the supernatant. These calculated results are presented in Figure 5.3.

The calculated sludge masses were determined by adding the solids removed during sampling and those lost in the supernatant to what was measured to be in the system, i.e. the calculated sludge mass at cycle 10 was the measured mass plus the mass of solids removed during sampling at cycle 5 plus the solids lost in the supernatant in cycles 1 to 10. The calculated sludge mass at cycle 15 was the measured mass plus the mass of solids removed during sampling at cycle 10 plus cycle 5 etc. Figure 5.3 shows that the calculated mass of sludge increases approximately linearly.

The calculated sludge volumes were determined by increasing the measured sludge volumes by the ratio of the calculated sludge mass to the measured sludge mass. i.e.

$$\text{Calculated sludge volume} = \text{Measured sludge volume} \times \frac{\text{Calculated sludge mass}}{\text{Measured sludge mass}}$$

The trend of the calculated sludge volume is more similar to the one predicted by Bosman (1983) (see Figure 5.1).

Figure 5.3 shows how the calculated sludge mass increased from circa 2.68 g after cycle 5, when the calculated sludge volume was 155 ml, to 17.0 g after cycle 35. During this period the calculated sludge volume had decreased by 12% to approximately 137 ml.

Theoretically, if the iron was removed as Fe (III) hydroxide, zinc as zinc hydroxide, aluminium as aluminium hydroxide and manganese as manganese oxy-hydroxide (see Table 2.7 Section 2.6.1) the solids would contain 35.5% iron and this would equate to a solid generation rate of 2.82 g of solids per g of iron removed. Using a total iron concentration of 199 mg/l in the feed water, the sludge generation rate would be 561 mg/l or a predicted total solids mass generated during the batch test would be 19.6 g dried solids.

Analysis of the sludge generated during the test indicated that 34.9% of the solid was iron, 7.6% was zinc, 3.1% was aluminium and 1.0% was manganese. Using the actual iron solid percentage of 34.9% a solids generation rate of 2.87 g of sludge per g of iron removed was calculated. Using the total iron concentration of 199 mg/l in the feed water, the actual sludge generation rate was 571 mg/l. Therefore, a total of approximately 20 g of solids would have been generated. The calculated mass of 17.0 g is 85% of predicted mass, and taking into account un-precipitated metals and error in analysis, though slightly low, represents an acceptable mass balance, see Section 3.5.

Figure 5.4 presents the equivalent sludge volume and mass data for the Denver flotation cell. As it has been established, the measured sludge volumes and measured sludge masses are an underestimation, therefore only the calculated volumes and calculated sludge masses will be discussed in the subsequent result sections. The calculated sludge volume trend line (5^{th} order polynomial), presented in Figure 5.4, (and all subsequent trend lines) was generated by the Excel spreadsheet package; this caused the increase in the trend line after the 34^{th} cycle.

The Denver test sludge concentrations are presented in Table 5.4 along with the supernatant and initial solids concentrations. In comparison to the Wemco flotation cell test, Figure 5.4 shows how the calculated sludge mass increased from circa 2.46 g after cycle 5, when the calculated sludge volume was 145 ml, to 15.6 g after cycle 35. During this period the calculated sludge volume had increased by 28% to approximately 185 ml.

The total mass of solids generated (sum of the measured mass of solids, the mass of solids removed during sampling and the mass of lost in the supernatant water) during the batch test was 15.6 g of dried solids or a solids generation rate of 446 mg of solids per litre of minewater treated. This indicates that the Wemco unit

produced an extra 39 mg/l of solids per cycle compared to the Denver unit, which is equivalent to an 8% increase in the sludge production rate. This increase in solids generation was likely to have been caused by the increased air flow rates in the Wemco unit (see Section 5.5), which resulted in increased carbonate production (see Section 5.6.2).

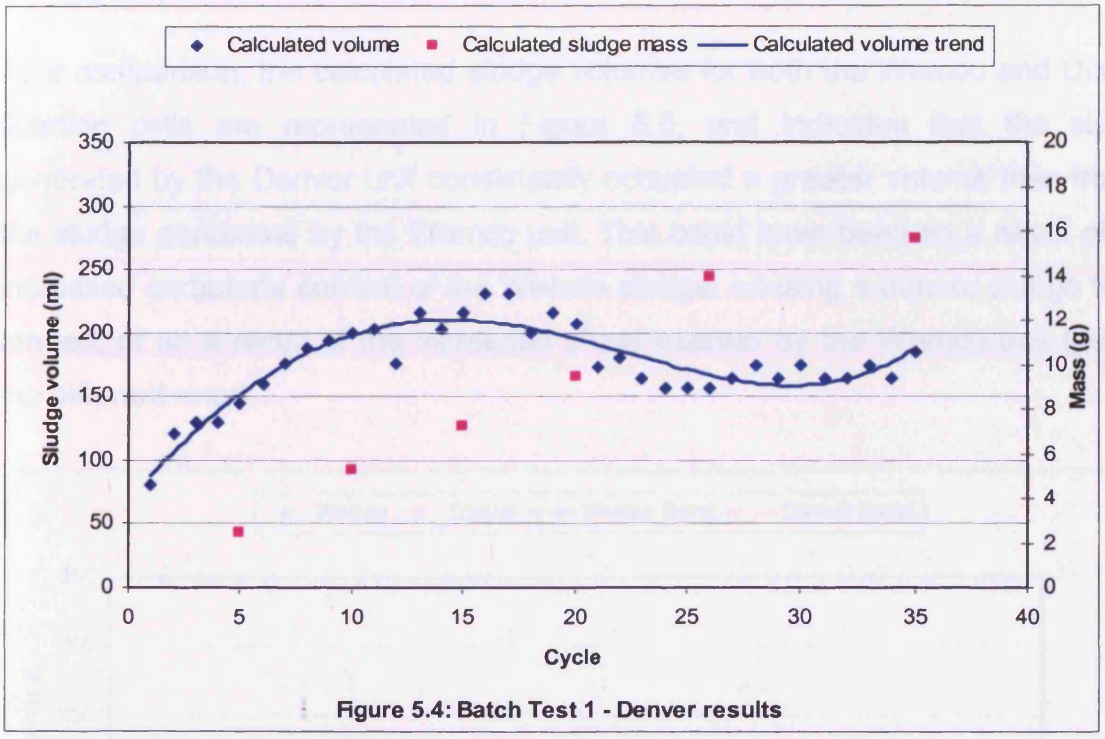


Figure 5.4: Batch Test 1 - Denver results

Table 5.4: Batch Test 1 Denver sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 20	Cycle 26	Cycle 35
Initial solids	g/l	2.1	3.9	4.7	5.4	8.1	7.0
Settled sludge solids	g/l	16.2	26.6	33.5	45.6	89.1	84.4
Supernatant solids	mg/l	22	57	83	120	99	84

As with the Wemco test, if the iron was removed as Fe (III) hydroxide, zinc as zinc hydroxide, aluminium as aluminium hydroxide and manganese as manganese oxy-hydroxide the theoretical sludge generation rate would be 561 mg/l, or the theoretical total solids mass generated during the batch test would be 19.6 g dried solids.

Analysis of the sludge generated during the test indicated that 38.9% of the solid was iron, 8.0 % was zinc, 3.5% was aluminium and 1.1% was manganese. Using the iron solid percentage of 38.9% a solids generation rate of 2.57 g of sludge per

g of iron removed was calculated. Using an iron concentration of 199 mg/l in the feed water, the sludge generation rate was 516 mg/l. Therefore a total of approximately 18 g of solids would have been anticipated. The calculated mass of 15.6 g is 87% of the predicted mass though, slightly low, is an acceptable mass balance when taking into account un-precipitated metals and analytical errors (see Section 3.5).

As a comparison, the calculated sludge volumes for both the Wemco and Denver flotation cells are represented in Figure 5.5, and indicates that the sludge generated by the Denver unit consistently occupied a greater volume than that of the sludge generated by the Wemco unit. This could have been as a result of the increased carbonate content of the Wemco sludge, causing a denser sludge to be formed, or as a result of the increased shear exerted by the Wemco unit (due to the different rotor).

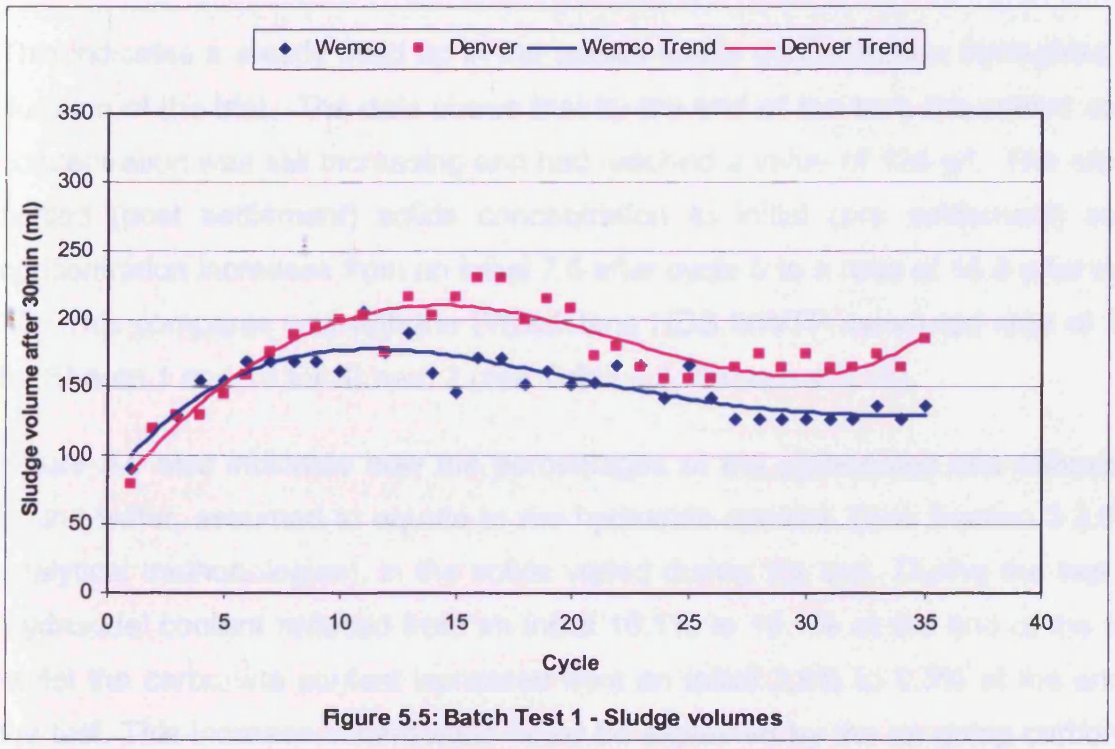


Figure 5.5: Batch Test 1 - Sludge volumes

5.6.2 Batch Test 1 – Sludge Composition

The variation in Wemco initial (pre settlement) and settled sludge (post settlement) solids concentration after 30 minutes is shown in Figure 5.6 and presented in Table 5.4.

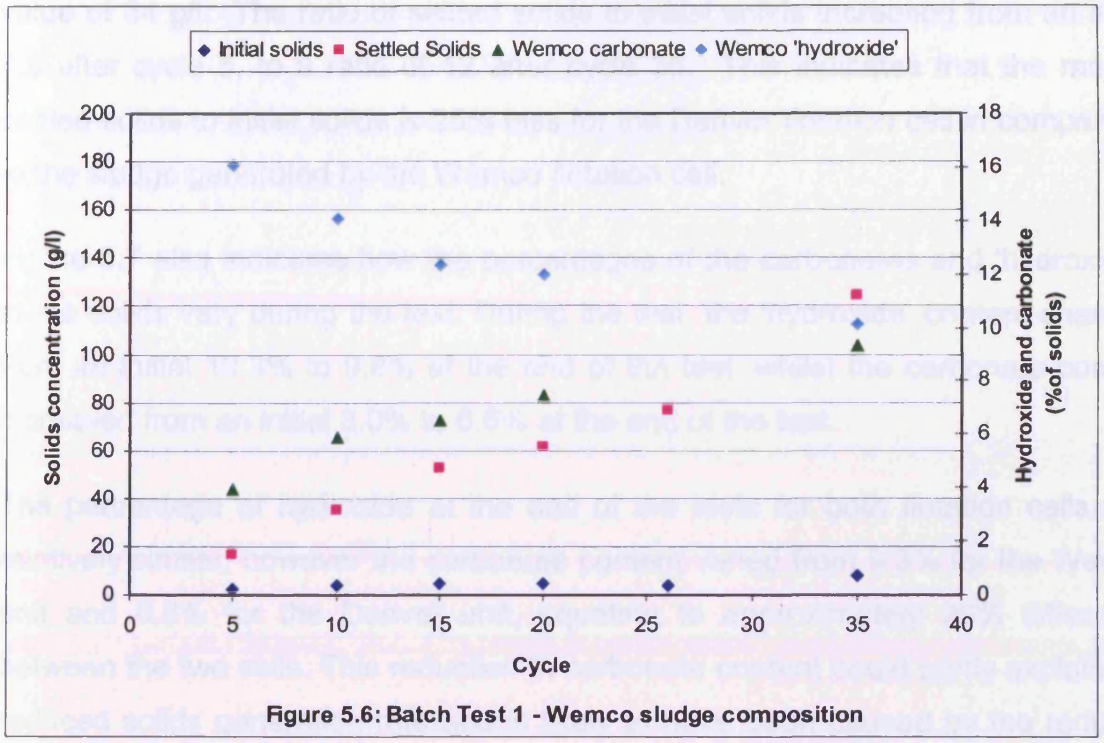


Figure 5.6: Batch Test 1 - Wemco sludge composition

This indicates a steady build up in the settled solids concentration throughout the duration of the trial. The data shows that by the end of the test, the settled solids concentration was still increasing and had reached a value of 124 g/l.. The ratio of settled (post settlement) solids concentration to initial (pre settlement) solids concentration increases from an initial 7.5 after cycle 5 to a ratio of 16.3 after cycle 35. This compares well with the Wheal Jane HDS MWTP measured ratio of 11.9 for Stream 1 and 13 for Stream 2 (see Table 4.8, Section 4.5.13).

Figure 5.6 also indicates how the percentages of the carbonates and chemically bound water, assumed to equate to the hydroxide content, (see Section 3.2.5 for analytical methodologies), in the solids varied during the test. During the test the 'hydroxide' content reduced from an initial 16.1% to 10.1% at the end of the test, whilst the carbonate content increased from an initial 3.9% to 9.3% at the end of the test. This increase in carbonate could be explained by the on going carbonate production, which is time dependant, during the batch test. Therefore, as the test continued, more carbonate was produced in proportion to the other constituents increasing the carbonate percentage in the sludge and decreasing the 'hydroxide' percentage.

The variation in Denver initial and settled solids concentration after 30 minutes is shown in Figure 5.7 and presented in Table 5.4. The data shown that by the end of the test, the settled solids concentration was still increasing and had reached a

value of 84 g/l. The ratio of settled solids to initial solids increased from an initial 7.8 after cycle 5, to a ratio of 12 after cycle 35. This indicates that the ratio of settled solids to initial solids is 25% less for the Denver flotation cell in comparison to the sludge generated by the Wemco flotation cell.

Figure 5.7 also indicates how the percentages of the carbonates and 'hydroxides' in the solids vary during the test. During the test, the 'hydroxide' content changed from an initial 10.3% to 9.8% at the end of the test, whilst the carbonate content increased from an initial 3.0% to 6.6% at the end of the test.

The percentage of hydroxide at the end of the tests for both flotation cells was relatively similar, however the carbonate content varied from 9.3% for the Wemco unit and 6.6% for the Denver unit, equating to approximately 29% difference between the two cells. This reduction in carbonate content could partly explain the reduced solids generation rate and is likely to have been caused by the reduced aeration rate in the Denver unit compared to the Wemco unit (see Section 5.5).

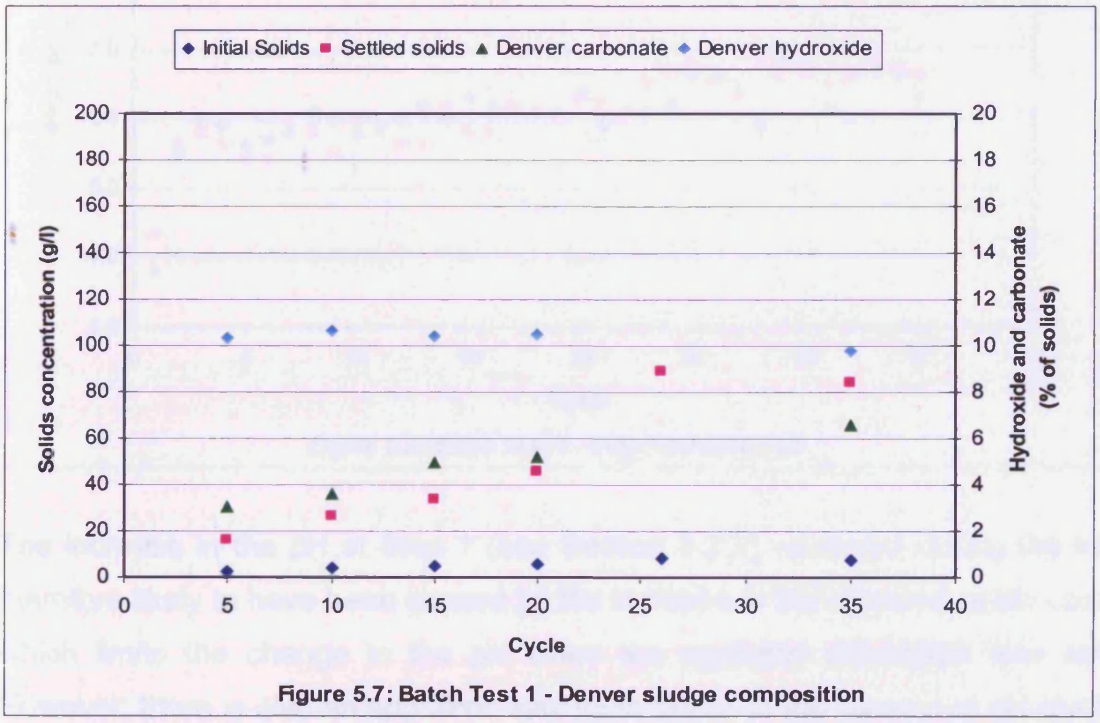


Figure 5.7: Batch Test 1 - Denver sludge composition

The mass balance undertaken does not take into account any phase changes of the solids generated.

5.6.3 Batch Test 1 – pH Readings

The pH was recorded during the test at three stages. These were:

1 As the fresh synthetic minewater was mixed with the recycled sludge at the start of Step 1 (Section 5.2.2).

2 Post mixing of the recycled sludge with the fresh minewater at the end of Step 2 (Section 5.2.2).

3 During and post aeration of the sludge/minewater mix, throughout Step 4 (Section 5.2.2).

The pH readings taken at the start of Step 1 are presented in Figure 5.8. These show a steady increase in the pH during the test from approximately 4, when no recycled solids were present at the start of the test, to circa 6.75, at the end of the test.

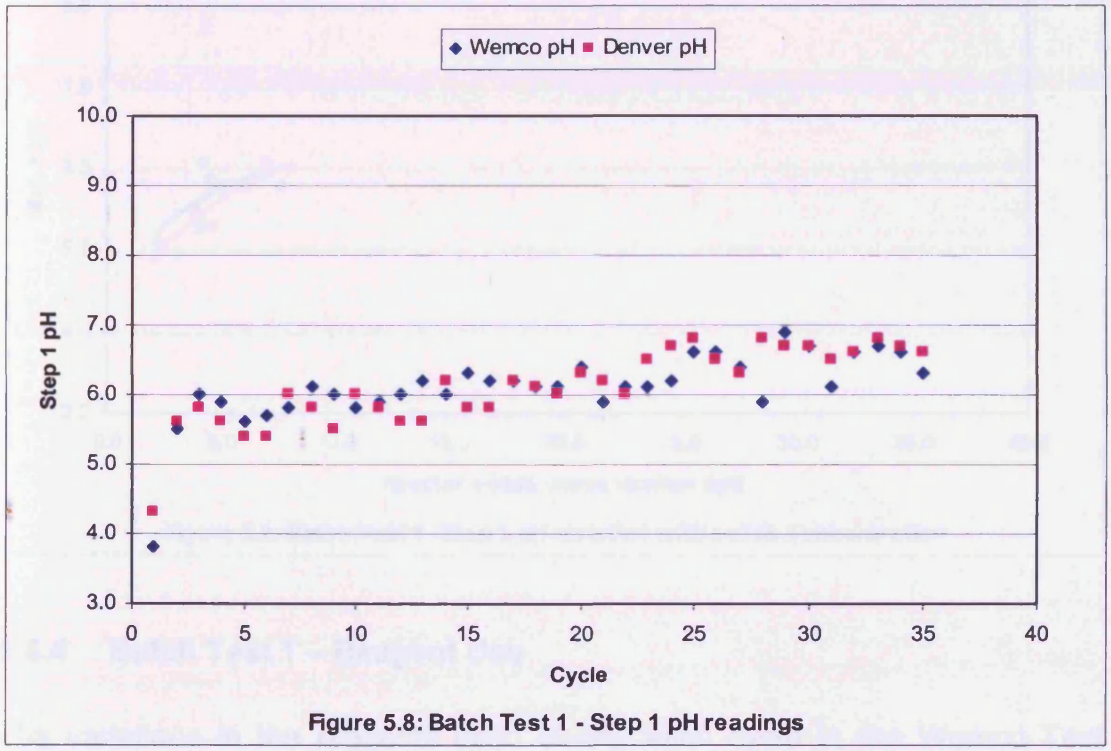


Figure 5.8: Batch Test 1 - Step 1 pH readings

The increase in the pH at Step 1 (see Section 5.2.2) observed during the test is therefore likely to have been caused by the increase in the recycled solids content, which limits the change in the pH when the synthetic minewater was added. However, there is also an apparent 'saw tooth effect' in the measured pH readings at Step 1. This 'saw tooth effect' is likely to have been caused by the removal of the 25 ml sludge samples every fifth cycle, enabling a greater change in the pH to occur after the addition of the fresh minewater. There is no apparent difference between the pH readings from the Denver and the Wemco flotation cells.

Experience has shown (see Chapter 6) that the amount of solids in the Stage I Reactor (equivalent to Step 1 in the batch test methodology, Section 5.2.2) helps

to control the pH post fresh minewater addition and can also affect the settleability of the sludge.

Figure 5.9 shows how the Step 1 pH varies with the reactor solids concentration. In general it can be seen that as the reactor solids concentration increases, the initial pH increases. This is likely to be due to the increased solids concentrations limiting the pH change.

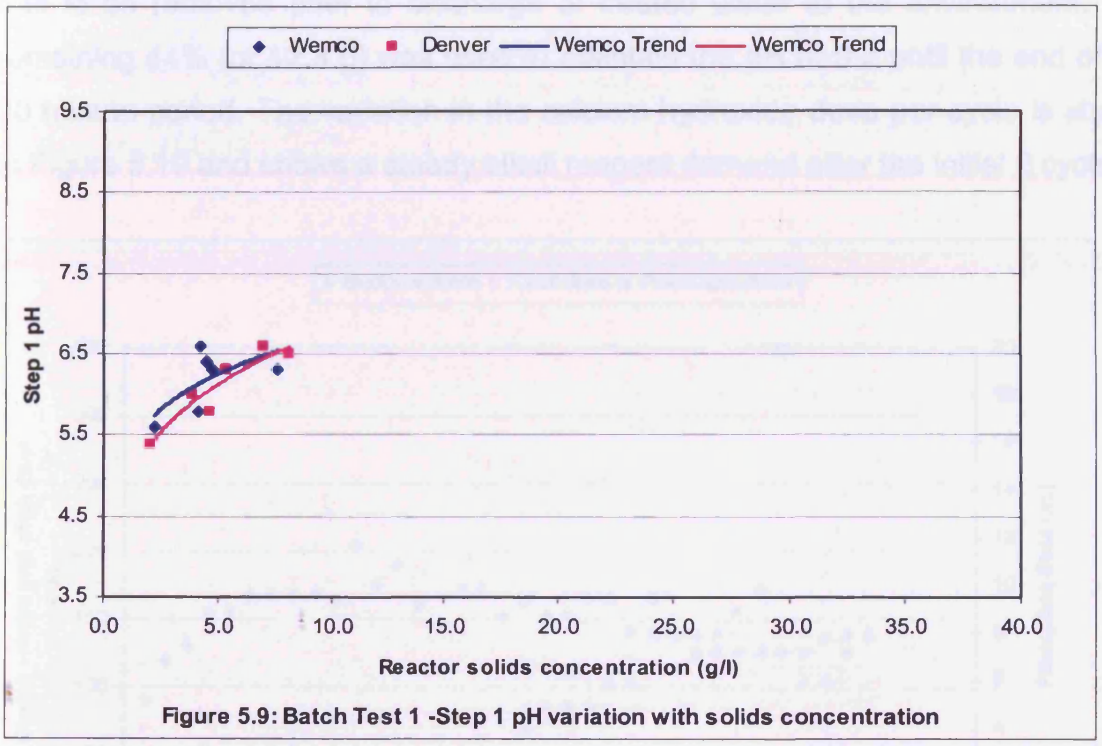


Figure 5.9: Batch Test 1 -Step 1 pH variation with solids concentration

5.6.4 Batch Test 1 – Reagent Use

The variations in the reagents used during each cycle in the Wemco Test are presented in Figure 5.10. The amount of alkali reagent, calcium hydroxide, added was recorded per cycle in ml (the calcium hydroxide was added as a slurry at approximately 22 g/l).

To enable the calcium hydroxide consumption to be calculated for the Wemco batch test, the total calcium hydroxide slurry added was calculated (1220 ml) and compared with the total metal removed. The total mass of calcium hydroxide added was 27.9 g, whilst the total mass of metal added was 10.3 g, giving a dose of 2.71 g of calcium hydroxide per g of metal removed. This compares to a theoretical dose of 1.53 g of calcium hydroxide per g of metal or an efficiency rate of 56.2% from the Wemco cell. The inefficiency in the calcium hydroxide dose was

likely to have been caused by the removal of CO_2 (input during aeration) from the system as carbonates. This was confirmed during the Denver batch test when less aeration occurred, resulting in less carbonate production and increased calcium hydroxide efficiency. It was observed that 56% (equivalent to 15.6 g) of the alkali reagent was used to raise the pH from the initial pH to the final pH of 9.2 and was achieved in an average of approximately 5 minutes. The final pH value of 9.2 was chosen as this is the operating pH at the Wheal Jane MWTP, where manganese has to be removed prior to discharge of treated water to the environment. The remaining 44% (or 12.3 g) was used to maintain the pH at 9.2 until the end of the 30 minute period. The variation in the calcium hydroxide dose per cycle is shown in Figure 5.10 and shows a steady alkali reagent demand after the initial 2 cycles.

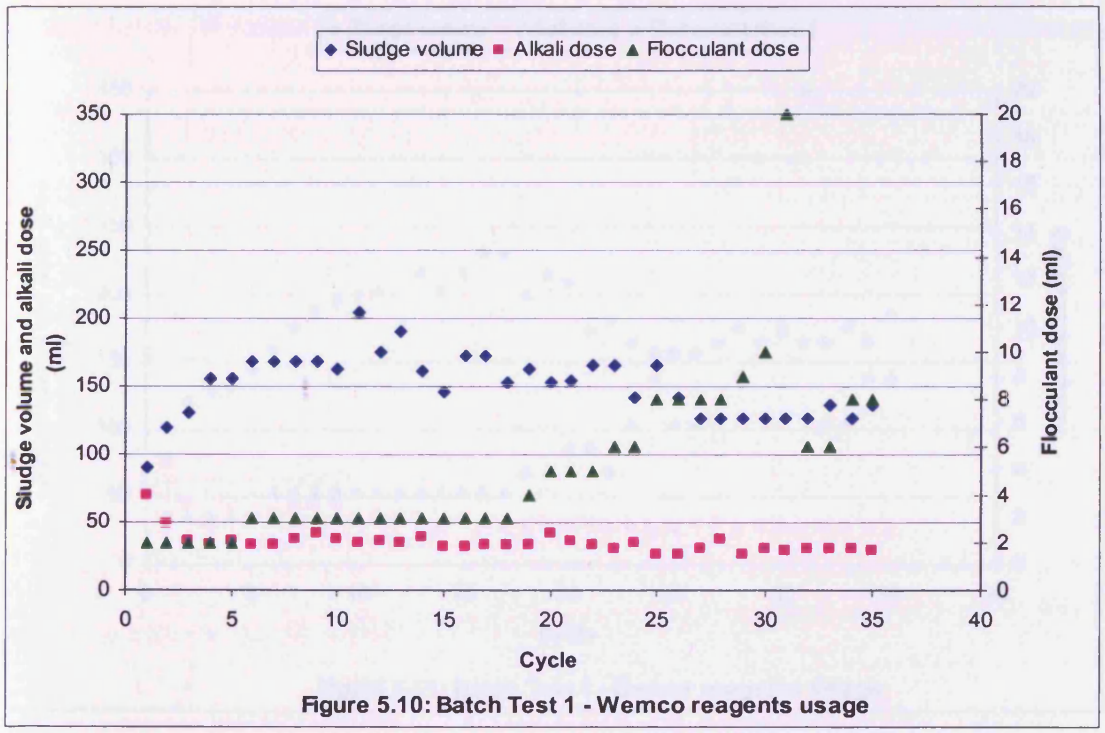


Figure 5.10: Batch Test 1 - Wemco reagents usage

The flocculant was made up at a concentration of 0.1% w/v, 1000 mg of active flocculant per litre of water. To enable the flocculant consumption to be calculated for the batch test, the total diluted flocculant added was calculated, 179 ml or 179 mg of active flocculant, and compared with the total water volume treated, which gave an average dose of 5.11 mg of active flocculant per litre of water treated. The flocculant dose added per cycle is shown in Figure 5.10.

The variations in the reagents used per cycle for the Denver Test are presented in Figure 5.11. As with the Wemco test, total calcium hydroxide slurry added was totalled (1140 ml) and compared with the total metal removed. The variation in the

calcium hydroxide dose per cycle is shown in Figure 5.11 and as with the Wemco cell shows a steady alkali reagent demand after the initial 2 cycles.

The total calcium hydroxide used, 26.1 g, was compared with the total metal removed, 10.3 g, giving a dose of 2.53 g of calcium hydroxide per g of metal removed. This compares to a theoretical dose of 1.53 g of calcium hydroxide per g of metal, or an efficiency rate of 60.1% from the Denver cell. It was observed that 73% (19.0 g) of the alkali reagent was used to raise the pH from the initial pH to the final pH of 9.2, and was achieved in an average of approximately 5.3 minutes. The remaining 28% (7.1 g) was used to maintain the pH at 9.2 until the end of the 30 minutes period.

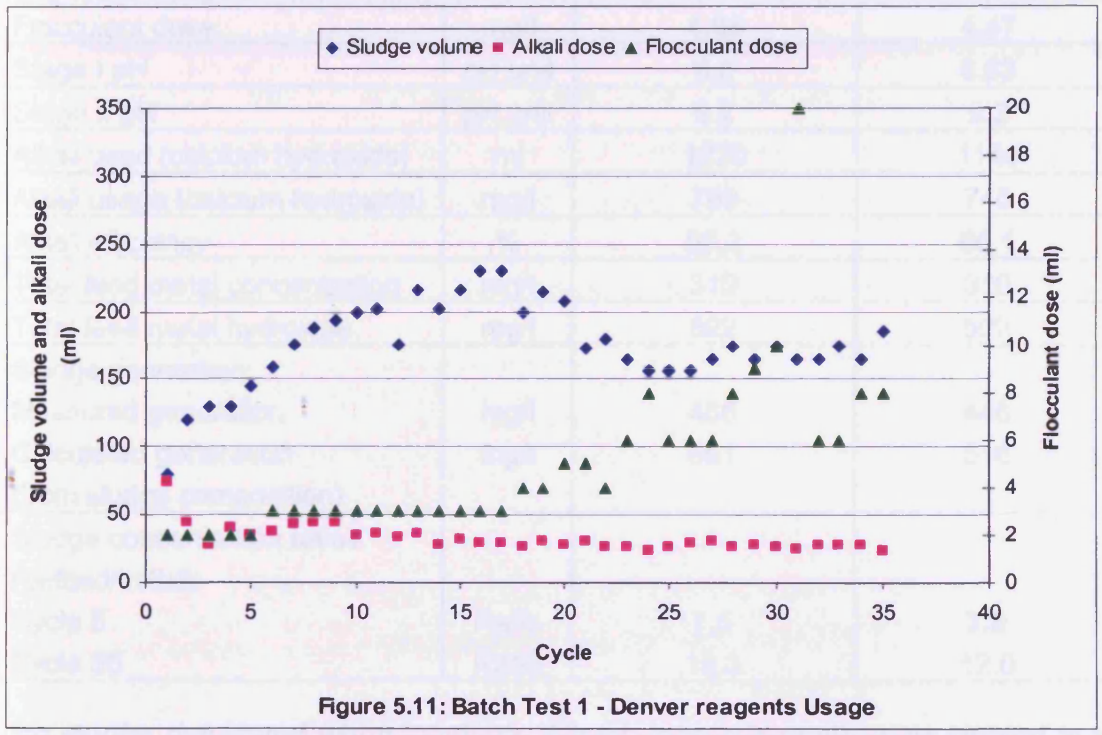


Figure 5.11: Batch Test 1 - Denver reagents Usage

Comparing the two flotation cells, 6.5% less alkali reagent was used during the Denver test in comparison to the Wemco test. However 21% (3.4 g) more was required to raise the pH from the initial pH to the desired pH of 9.2. This could be explained by the reduced carbonate content of the Denver sludge and hence a reduced buffering capacity of the sludge.

As with the Wemco test, the total diluted flocculant added was totalled, 175 ml or 175 mg of active flocculant, and compared with the total water volume treated, which gave an average dose of 5 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.11.

5.6.5 Batch Test 1 – Summary of Key Performance Parameters

The key performance indicators of Batch Test 1 are presented in Table 5.5.

Table 5.5: Batch Test 1 Key Performance Parameters

Parameter	Unit	Wemco Flotation Cell	Denver Flotation Cell
Maximum sludge Volume	ml	205	231
No of Cycles (max volume)	No	11	16
Minimum sludge Volume	ml	126	157
No of Cycles (Min volume)	No	27	24
Final Sludge Concentration	g/l	124	84.4
% of solid as Carbonate	%	9.3	6.6
% of solid as Hydroxide	%	10.1	9.8
Flocculant dose	mg/l	4.68	4.47
Stage I pH	pH unit	6.5	6.63
Stage II pH	pH unit	9.2	9.2
Alkali used (calcium hydroxide)	ml	1220	1140
Alkali usage (calcium hydroxide)	mg/l	798	746
Alkali efficiency	%	56.2	60.1
Total feed metal concentration	mg/l	310	310
Total feed metal hydroxide	mg/l	592	592
Sludge generation: Measured generation Calculated generation (from sludge composition)	 mg/l mg/l	 485 561	 446 516
Sludge concentration ratios (Settled/Initial) Cycle 5 Cycle 35	 Ratio Ratio	 7.5 16.3	 7.8 12.0

The sludge generated when synthetic Wheal Jane minewater was treated in both the Wemco and Denver flotation cells when calcium hydroxide was used as the alkali reagent exhibited similar reductions in sludge volumes as described by Bosman (Figure 5.1). Therefore, it is concluded that both the Wemco and Denver flotation cells formed HDS sludge.

After cycle 35 of the Wemco test, the ratio of settled sludge concentration to initial sludge concentration, and hence volumes, was 16.3 compared to a ratio of 7.5 after cycle 5.

The ratio of settled sludge concentration to initial sludge concentration for the Denver cell after cycle 35 was 12.0, slightly lower than the 16.3 for the Wemco

cell, hence a less densely settling sludge was formed. This was likely to have been caused by either the extra shearing exerted on the sludge by the Wemco cell or, the higher carbonate composition to the sludge, as a result of the increased air flowrate in the Wemco cell compared to the Denver cell, see Section 5.5. The Wheal Jane HDS MWTP measured ratio of between 11.9 and 13 compares well with the ratios measured during Batch Test 1 hence it is concluded that the batch test results are comparable to the results obtained from the full-scale Wheal Jane HDS MWTP.

5.7 Batch Test 2 – Synthetic Wheal Jane Minewater treated with Sodium Hydroxide

The results of the subsequent batch tests (tests 2 to 9) are presented in the same way as 'Batch Test 1 - Synthetic Wheal Jane Minewater treated with calcium hydroxide' but eliminating certain plots as discussed. To limit repeated comments, the results are presented with summary comments where appropriate.

During Batch Test 2, 38 cycles were undertaken with the feed water and treated water, as presented in Table 5.6. The pH of the treated water of 1.4 was due to the treated water being acidified with sulphuric acid prior to analysis, which resulted in high a sulphate concentration, which also resulted in the high sulphate result.

Table 5.6: Batch Test 2 Water Quality Summary

Sample	pH	Solids mg/l	Fe mg/l	SO_4 mg/l	Ca mg/l	Zn mg/l	Al mg/l
Feed water	2.0	166	199	216	<1	63	25
Treated Water	1.4	96	12	19600	5	4.6	3.7

5.7.1 Batch Test 2 – Sludge Volume and Mass of Solids

Presented in Figure 5.12 is how the calculated sludge mass in the system and the calculated sludge volume varied with the number of cycles for the Wemco flotation cell. The sludge concentrations are presented in Table 5.7 along with the supernatant and initial solids concentrations. Figure 5.12 shows how the calculated sludge mass increased from circa 2.69 g after cycle 5, when the calculated sludge volume was 220 ml, to 15.8 g after cycle 35. During this period, the calculated sludge volume had increased by 13% to approximately 248 ml.

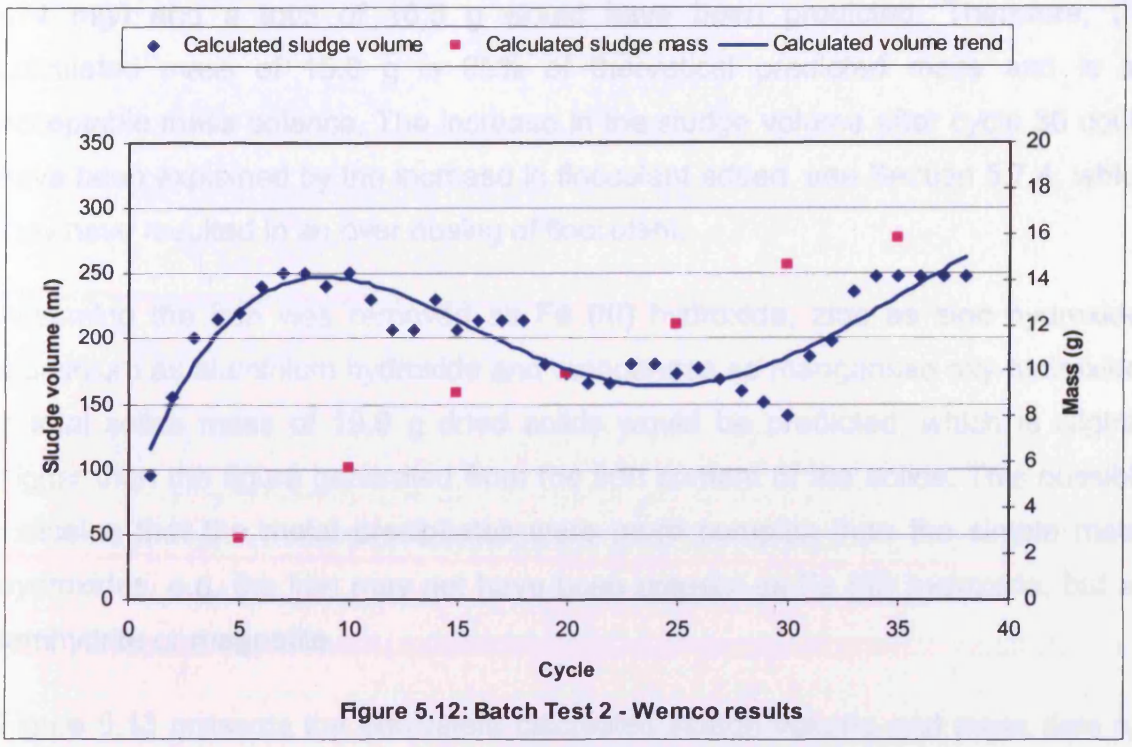


Figure 5.12: Batch Test 2 - Wemco results

Table 5.7: Batch Test 2 Wemco sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 20	Cycle 25	Cycle 30	Cycle 35
Initial solids	g/l	2.17	4.30	6.57	6.54	7.16	7.64	5.81
Settled sludge solids	g/l	12.01	23.0	43.8	57.1	69.7	104	64.0
Supernatant solids	mg/l	11	23	37	39	31	110	100

The total mass of solids generated during the test was 15.8 g of dried solids or a solids generation rate of 452 mg of solids per litre of minewater treated.

The total suspended solids in the supernatant increased dramatically after cycle 30. To overcome this, the flocculant dose was increased, see Section 5.7.4. However, this resulted in further increasing the total suspended solids concentration and in reality the flocculant dose should have been reduced not increased.

Analysis of the sludge generated during the Wemco batch test total mass balance indicated that 41.9% of the solid was iron, 8.7% was zinc, 3.6% was aluminium and 1.5% was manganese. Using the iron solid percentage of 41.9%, a solids generation rate of 2.39 g of sludge per g of iron removed was calculated. Using an iron concentration of 199 mg/l in the feed water, the sludge generation rate was

474 mg/l and a total of 16.6 g would have been predicted. Therefore, the calculated mass of 15.8 g is 95% of theoretical predicted mass and is an acceptable mass balance. The increase in the sludge volume after cycle 30 could have been explained by the increase in flocculant added, see Section 5.7.4, which may have resulted in an over dosing of flocculant.

Assuming the iron was removed as Fe (III) hydroxide, zinc as zinc hydroxide, aluminium as aluminium hydroxide and manganese as manganese oxy-hydroxide, a total solids mass of 19.6 g dried solids would be predicted, which is slightly higher than the figure generated from the iron content of the solids. This possibly indicates that the metal precipitates were more complex than the simple metal hydroxides, e.g. the iron may not have been present as Fe (III) hydroxide, but as ferrihydrite or magnetite.

Figure 5.13 presents the equivalent calculated sludge volume and mass data for the Denver flotation cell. The sludge concentrations are presented in Table 5.8 along with the supernatant and initial solids concentrations.

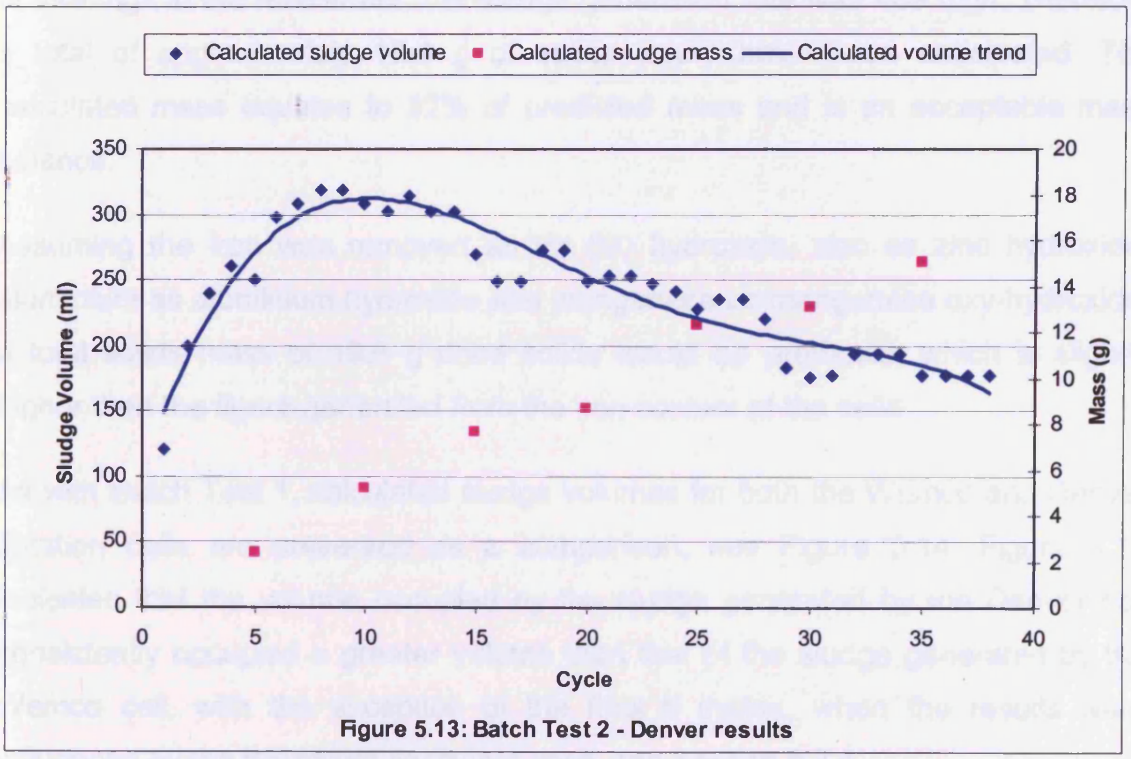


Figure 5.13: Batch Test 2 - Denver results

Table 5.8: Batch Test 2 Denver sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 20	Cycle 25	Cycle 30	Cycle 35

Initial solids	g/l	1.82	3.79	5.37	5.76	8.17	7.97	7.71
Sludge solids	g/l	9.16	17.0	28.4	35.2	54.0	74.7	85.5
Supernatant solids	mg/l	12	5	19	29	9	43	100

In comparison to the Wemco flotation cell test, Figure 5.14 shows how the calculated sludge mass increased from circa 2.35 g after cycle 5, when the calculated sludge volume was 250 ml, to 15.1 g after cycle 35. During this period, the calculated sludge volume had decreased by 30% to approximately 177 ml.

The total mass of solids generated during the test was 15.1 g of dried solids, or a solids generation rate of 432 mg of solids per litre of minewater treated. This indicates that the Wemco cell produced an extra 21 mg/l of solids per cycle, which is equivalent to 5% increase in the sludge production rate.

Analysis of the sludge generated during the Denver batch test indicated that 42.4% of the solid was iron, 8.9% was zinc, 3.9% was aluminium and 1.6% was manganese. Using the iron solid percentage of 42.4% a solids generation rate of 2.36 g of sludge per g of iron removed was calculated. Using an iron concentration of 199 mg/l in the feed water, the sludge generation rate was 469 mg/l. Therefore a total of approximately 16.4 g of solids would have been anticipated. The calculated mass equates to 92% of predicted mass and is an acceptable mass balance.

Assuming the iron was removed as Fe (III) hydroxide, zinc as zinc hydroxide, aluminium as aluminium hydroxide and manganese as manganese oxy-hydroxide, a total solids mass of 19.6 g dried solids would be predicted, which is slightly higher than the figure generated from the iron content of the solid.

As with Batch Test 1, calculated sludge volumes for both the Wemco and Denver flotation cells are presented as a comparison, see Figure 5.14. Figure 5.14 indicates that the volume occupied by the sludge generated by the Denver cell consistently occupied a greater volume than that of the sludge generated by the Wemco cell, with the exception of the final 5 cycles, when the results were influenced by the increased flocculant dose, see Section 5.7.4.

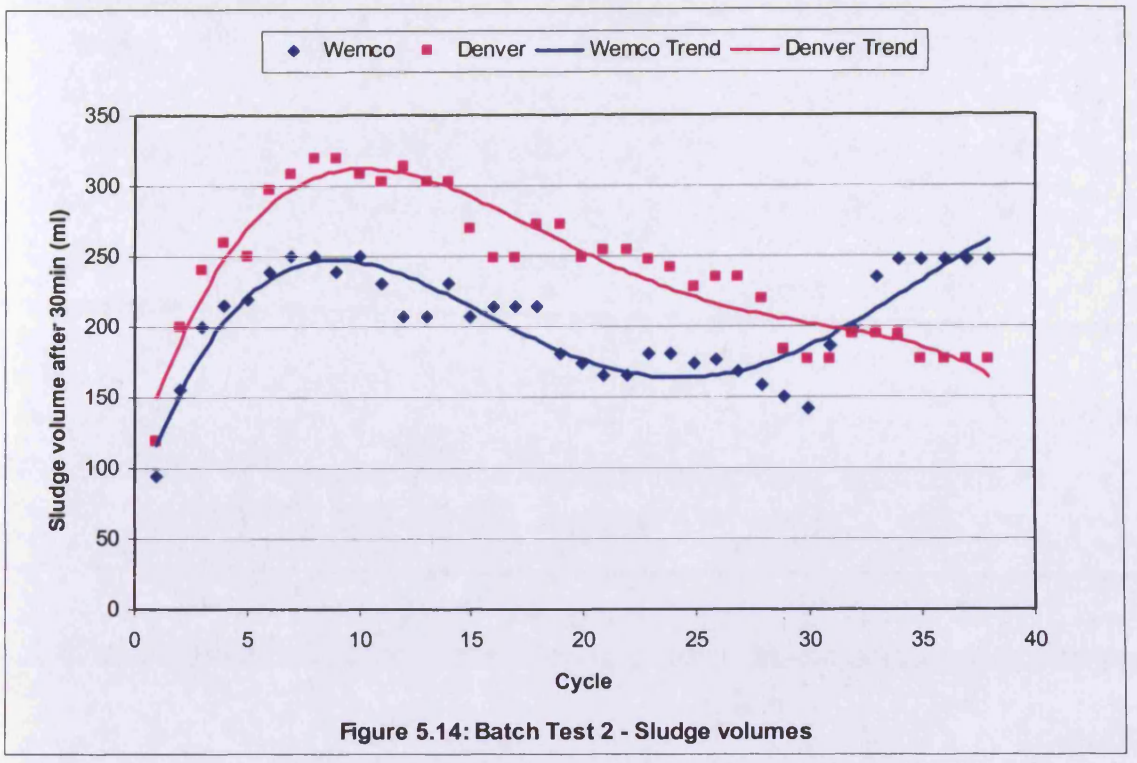


Figure 5.14: Batch Test 2 - Sludge volumes

5.7.2 Batch Test 2 – Sludge Composition

The variation in Wemco initial and settled sludge solids concentration after 30 minutes is shown in Figure 5.15 and presented in Table 5.7.

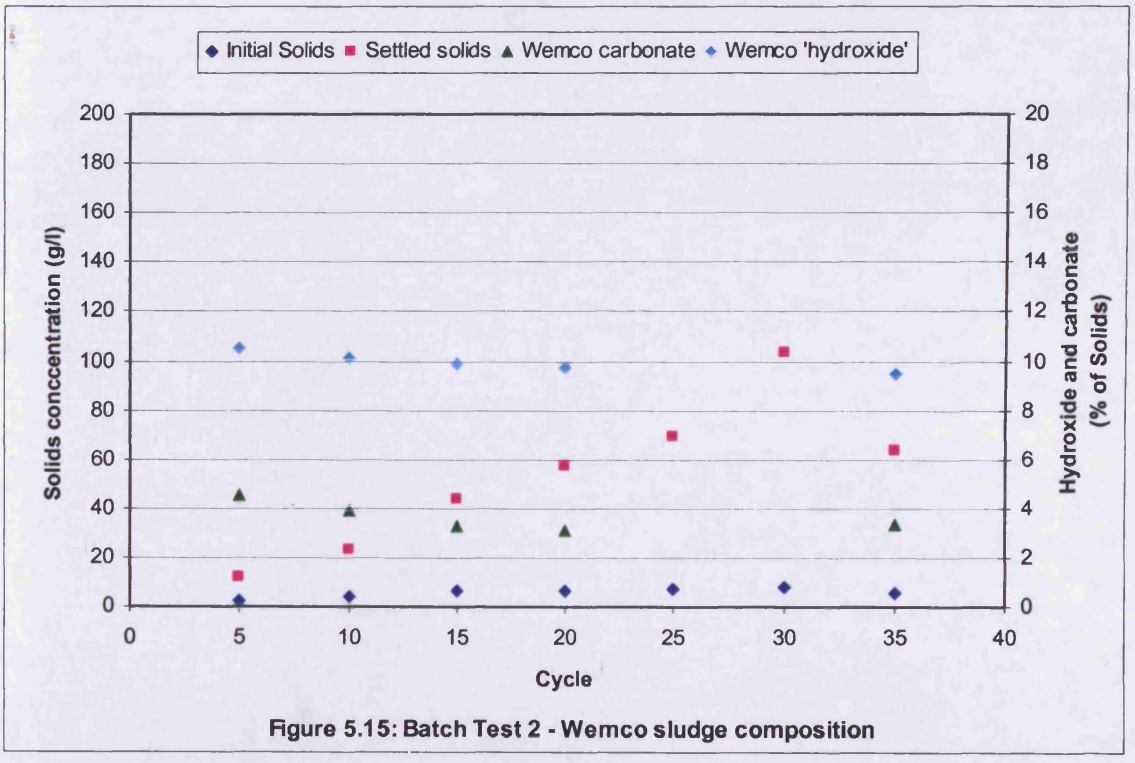


Figure 5.15: Batch Test 2 - Wemco sludge composition

This indicates a steady build up in the settled solids concentration up to cycle 30.

The settled solids concentration decreased by cycle 35 due to the reduced settled volume as a result of the other dosing of flocculant, see Section 5.74. The data shows that by the end of the test, the settled solids concentration was still increasing and had reached a peak value of 104 g/l. The ratio of settled sludge solids to initial sludge solids increases from an initial 5.5 after cycle 5 to a ratio of 13.6 after cycle 30.

Figure 5.15 also indicates how the percentages of the carbonates and 'hydroxides' in the solids vary during the test. During the test the 'hydroxide' content reduced from an initial 10.5% to 9.5% at the end of the test, whilst the carbonate content had also decreased from an initial 4.6% to 3.4% by the end of the test.

The variation in Denver initial and settled solids concentration is shown in Figure 5.16 and presented in Table 5.8.

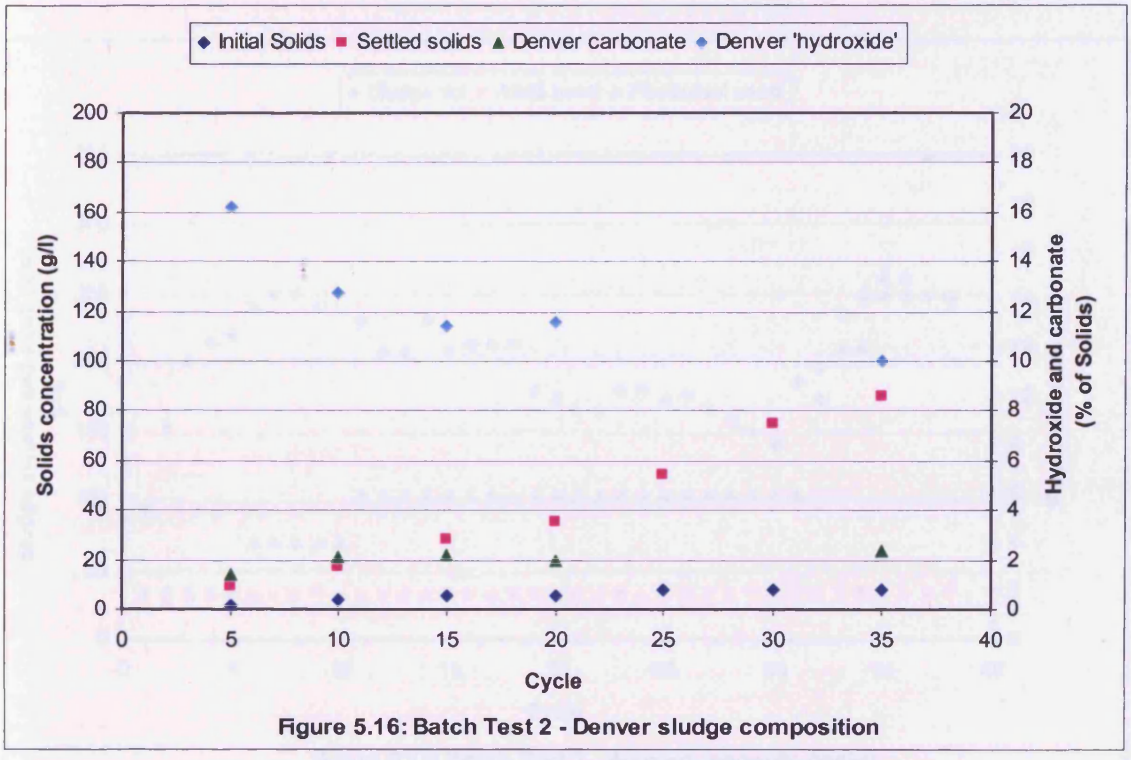


Figure 5.16: Batch Test 2 - Denver sludge composition

The ratio of settled solids to initial solids increases from an initial 5.0 after cycle 5 to a ratio of 11.1 after cycle 35. This indicates that the ratio of settled solids to initial solids is comparable between the two flotation cells.

Figure 5.16 also indicates how the percentages of the carbonates and 'hydroxides' in the solids vary during the test. During the test, the 'hydroxide' content changed from an initial 16.2% to 10.0% at the end of the test, whilst the carbonate content

increased from an initial 1.4% to 2.4% at the end of the test. The percentage of chemically bound water at the end of the tests for both flotation cells was relatively similar, however the carbonate content varied from 3.4% for the Wemco cell and 2.4% for the Denver cell, equating to approximately 29% difference between the two cells. As with Batch Test 1, this was likely to have been caused by the different aeration rates.

5.7.3 Batch Test 2 – pH Readings

No pH readings were taken during Batch Test 2.

5.7.4 Batch Test 2 – Reagent Use

The variations in the reagents used per cycle for the Wemco Test are presented in Figure 5.17 and shows a steady alkali reagent demand throughout the batch test.

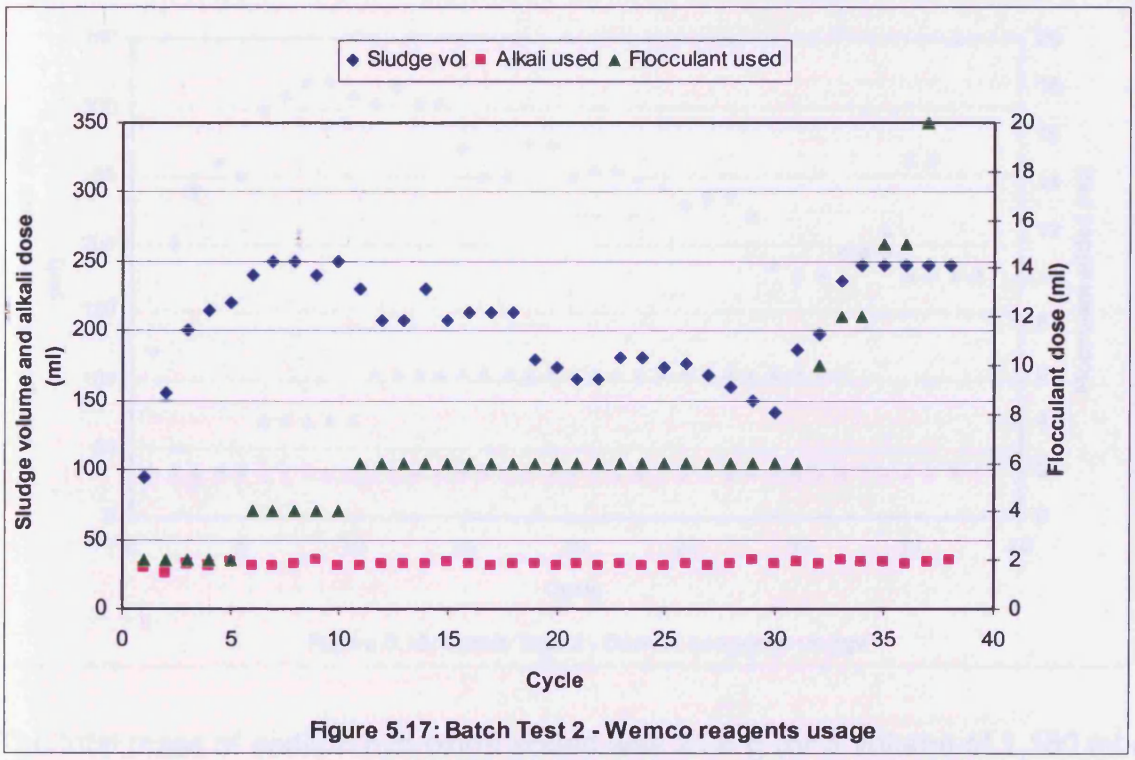


Figure 5.17: Batch Test 2 - Wemco reagents usage

The amount of alkali reagent, sodium hydroxide, added was recorded per cycle in ml (the sodium hydroxide was added as a solution at approximately 20 g/l). The total mass of sodium hydroxide added was 23.7 g (or a volume of 1,190 ml of solution), whilst the total mass of metal added was 10.3 g giving a dose of 2.3 g of sodium hydroxide per g of metal removed. This compares to a theoretical dose of 1.64 g of sodium hydroxide per g of metal or an efficiency rate of 71.5% from the

Wemco cell.

During Batch Test 2, 240 ml or 240 mg of active flocculant was added, and compared with the total water volume treated, giving an average dose of 5.53 mg of active flocculant per litre of water treated. The variation in the flocculant dose during the batch test is shown in Figure 5.17, where the dose increased from approximately 6 ml after cycle 31 to approximately 20 ml after cycle 38. The dose was increased as a result of increasing supernatant suspended solids. However, a decrease in the dose may have been more appropriate.

The variations in the reagents used per cycle for the Denver Test are presented in Figure 5.18 and similarly to the Wemco cell shows a steady alkali reagent demand throughout the batch test.

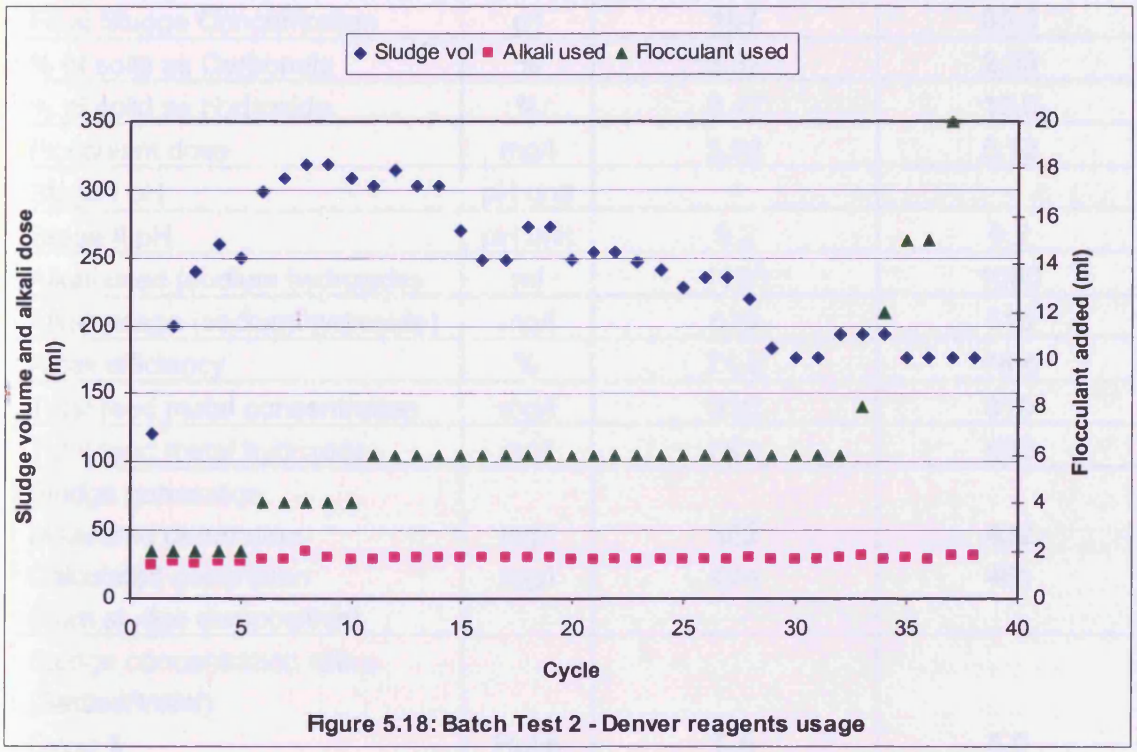


Figure 5.18: Batch Test 2 - Denver reagents usage

The total mass of sodium hydroxide added was 21.6 g (or a volume of 1,180 ml of solution), whilst the total mass of metal added was 10.3 g, giving a dose of 2.1 g of sodium hydroxide per g of metal removed. This compares to a theoretical dose of 1.64 g of sodium hydroxide per g of metal, or an efficiency rate of 78.4% from the Wemco cell. The variation in the sodium hydroxide dose per cycle is shown in Figure 5.18.

During Batch Test 2, 232 ml or 232 mg of active flocculant was added, and compared with the total water volume treated, giving an average dose of 5.12 mg

of active flocculant per litre of water treated. The variation in the flocculant dose during the batch test is shown in Figure 5.18. As with the Wemco cell an overdosing of flocculant occurred during the final 5 cycles.

5.7.5 Batch Test 2 – Summary of Key Performance Parameters

The key performance indicators of Batch Test 2 are presented in Table 5.9.

Table 5.9: Batch Test 2 Key Performance Parameters

Parameter	Unit	Wemco Flotation Cell	Denver Flotation Cell
Maximum sludge Volume	ml	250	319
No of Cycles (max volume)	No	7	7
Minimum sludge Volume	ml	141	176
No of Cycles (Min volume)	No	30	30
Final Sludge Concentration	g/l	104	85.5
% of solid as Carbonate	%	3.37	2.38
% of solid as Hydroxide	%	9.47	10.0
Flocculant dose	mg/l	5.53	5.12
Stage I pH	pH unit	-	-
Stage II pH	pH unit	9.2	9.2
Alkali used (sodium hydroxide)	ml	1190	1080
Alkali usage (sodium hydroxide)	mg/l	678	618
Alkali efficiency	%	71.5	78.4
Total feed metal concentration	mg/l	310	310
Total feed metal hydroxide	mg/l	592	592
Sludge generation: Measured generation Calculated generation (from sludge composition)	 mg/l mg/l	 452 474	 432 461
Sludge concentration ratios (Settled/Initial) Cycle 5 Cycle 35	 Ratio Ratio	 5.5 11.0	 5.0 11.1

As with Batch Test 1, the sludge generated during Batch Test 2, when sodium hydroxide was used as the alkali reagent, exhibited similar reductions in sludge volumes, as described by Bosman (Figure 5.1). Therefore, it is concluded that both the Wemco and Denver flotation cells formed HDS sludge.

After cycle 35 of the Wemco test, the ratio of settled (post settlement) sludge concentration to initial (pre settlement) sludge concentration, and hence volumes, was 11.0 compared to a ratio of 5.5 after cycle 5.

The Denver settled (post settlement) sludge concentration to initial (pre settlement) sludge concentration after cycle 35 was 11.1, comparable with the ratio for the sludge generated by the Wemco cell.

5.8 Batch Test 3 – Synthetic Wheal Jane Minewater Treated with Magnesium Hydroxide

During Batch Test 3, 37 cycles were undertaken with the feed water and treated water, as presented in Table 5.10 .

Table 5.10: Batch Test 3 Water Quality Summary

Sample	PH	Solids Mg/l	Fe mg/l	SO_4 mg/l	Ca mg/l	Zn mg/l	Al mg/l
Feed Water	2.0	166	199	216	<1	63	25
Treated Water	7.4	67	12	597	20	3.5	2.9

5.8.1 Batch Test 3 – Sludge Volume and Mass of Solids

Presented in Figure 5.19 is how the sludge mass in the system and the sludge volume varied with number of cycles for the Wemco flotation cell. The sludge concentrations are presented in Table 5.11 along with the supernatant and initial solids concentrations.

Table 5.11: Batch Test 3 Wemco Sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 25	Cycle 30	Cycle 35	Cycle 37
Initial solids	g/l	16.7	20.4	24.7	30.0	35.3	33.1	32.7
Sludge solids	g/l	240	246	269	253	298	311	305
Supernatant solids	mg/l	79	71	64	82	67	112	112

Figure 5.19 shows how the calculated sludge mass increased from circa 18.4 g after cycle 5, when the calculated sludge volume was 75 ml, to 80.1 g after cycle 37. During this period the calculated sludge volume had increased to approximately 262 ml. It is suggested that due to magnesium hydroxide being unable to raise the pH to above 9 efficiently, the magnesium hydroxide was overdosed during the batch test, see Section 5.8.4. This resulted in unreacted magnesium hydroxide being present in the sludge generated during the batch test, see Section 5.8.2, and a very large mass of sludge being generated.

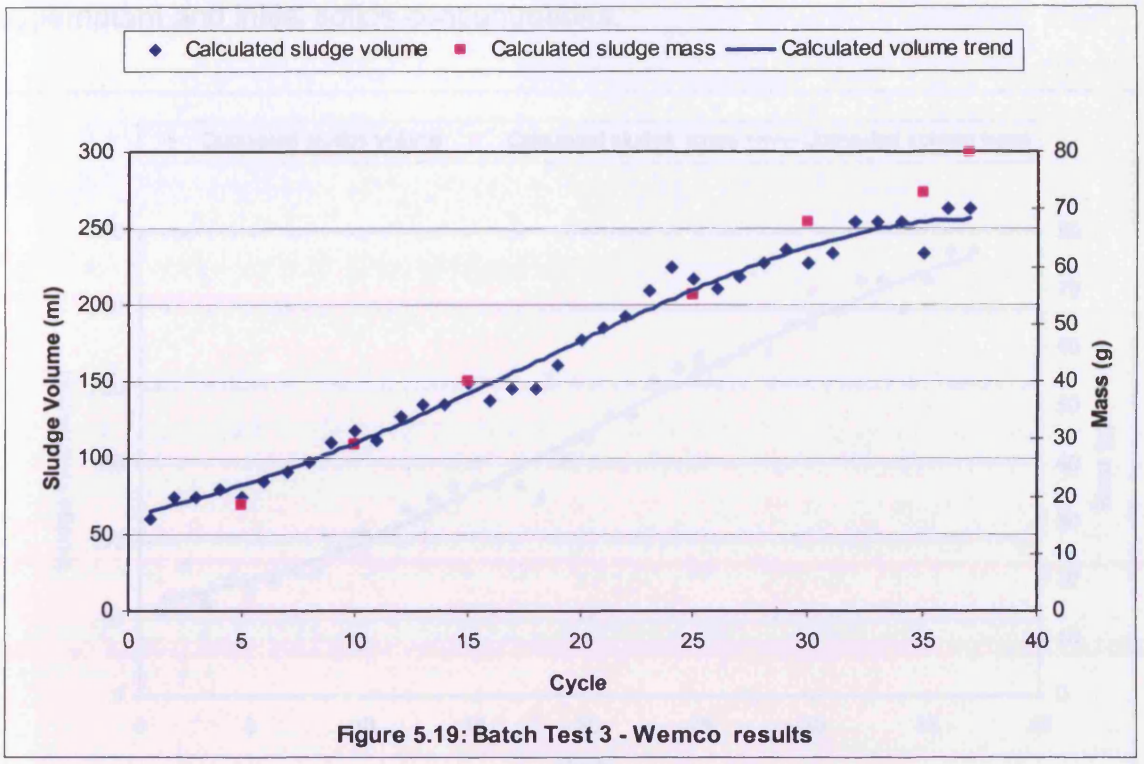


Figure 5.19: Batch Test 3 - Wemco results

The total mass of solids generated during the test was 80.1 g of dried solids or a solids generation rate of 2,160 mg of solids per litre of minewater treated.

Analysis of the final sludge generated during the test indicated that 12.4% of the solid was iron, 2.5% was zinc, 1.2% was aluminium and 0.3% was manganese. Using the iron solid percentage of 12.4%, a solids generation rate of 8.06 g of sludge per g of iron removed was calculated. Using an iron concentration of 199 mg/l in the feed water, the sludge generation rate was 1,610 mg/l. Therefore, a total of approximately 59.4 g of solids would have been anticipated after the full 37 cycles. The calculated mass equates to 135% of predicted mass. This imbalance was likely to have resulted from the overdosing of the magnesium hydroxide that occurred during the batch test.

Assuming the iron was removed as Fe (III) hydroxide, zinc as zinc hydroxide, aluminium as aluminium hydroxide and manganese as manganese oxy-hydroxide, a total solids mass of 20.8 g dried solids would be predicted. There is a clear imbalance, with the excess being as a result of unreacted magnesium hydroxide in the sludge. The inflated 'hydroxide' concentrations in the sludge would indicate that this is the case (see Section 5.8.2).

Figure 5.20 presents the equivalent sludge volume and mass data for the Denver flotation cell. The sludge concentrations are presented in Table 5.12 along with the

supernatant and initial solids concentrations.

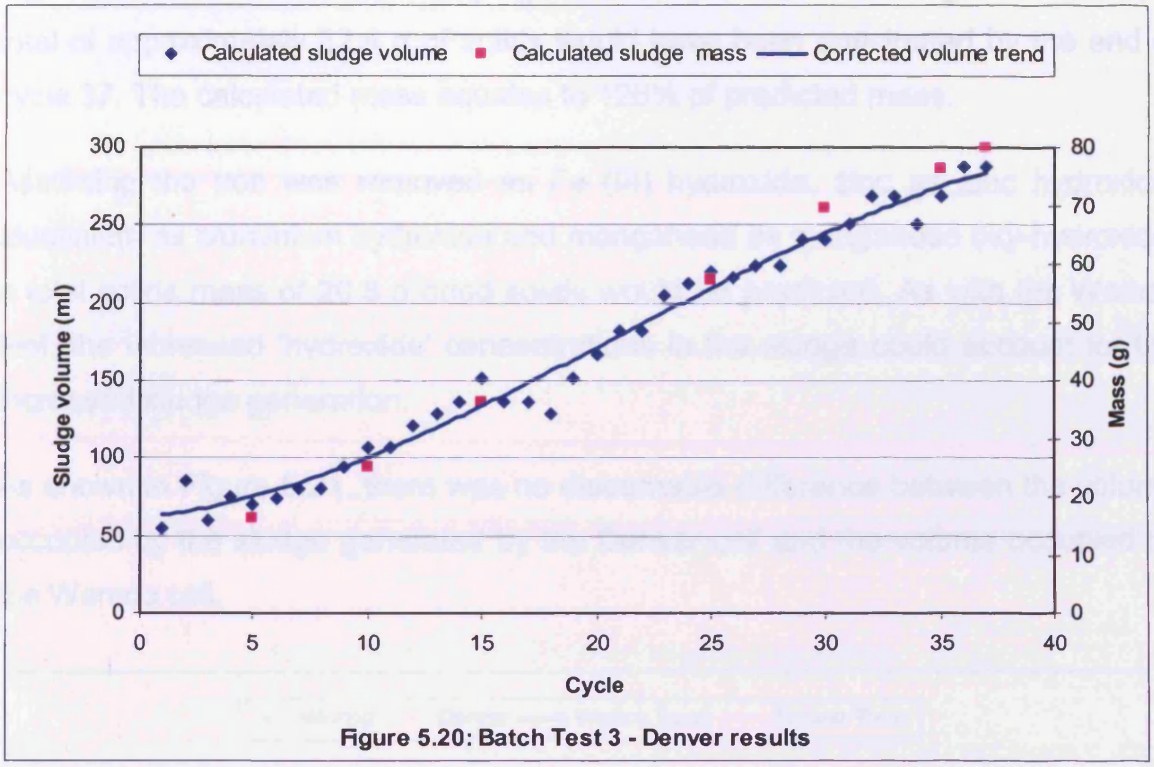


Figure 5.20: Batch Test 3 - Denver results

Table 5.12: Batch Test 3 Denver sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 25	Cycle 30	Cycle 35	Cycle 37
Initial solids	g/l	15.0	17.4	21.9	33.1	37.7	37.5	34.2
Sludge solids	g/l	230	233	239	260	289	285	278
Supernatant solids	mg/l	68	47	43	107	47	61	61

In comparison to the Wemco flotation cell test, Figure 5.20 shows how the calculated sludge mass increased from circa 16.4 g after cycle 5, when the calculated sludge volume was 70 ml, to 79.9 g after cycle 37. During this period the calculated sludge volume had increased to approximately 287 ml.

The total mass of solids generated during the test was 79.9 g of dried solids or a solids generation rate of 2,160 mg of solids per litre of minewater treated. This indicates that the Wemco cell produced an extra 6 mg/l of solids per cycle, which is equivalent to a 0.3% increase in the sludge production rate.

Analysis of the final sludge generated during the test indicated that 11.8% of the solid was iron, 2.4% was zinc, 1.1% was aluminium and 0.3% was manganese. Using the iron solid percentage of 11.8% a solids generation rate of 8.47 g of

sludge per g of iron removed was calculated. Using an iron concentration of 199 mg/l in the feed water, the sludge generation rate was 1690 mg/l. Therefore, a total of approximately 62.4 g of solids would have been anticipated by the end of cycle 37. The calculated mass equates to 128% of predicted mass.

Assuming the iron was removed as Fe (III) hydroxide, zinc as zinc hydroxide, aluminium as aluminium hydroxide and manganese as manganese oxy-hydroxide, a total solids mass of 20.8 g dried solids would be predicted. As with the Wemco test, the increased 'hydroxide' concentrations in the sludge could account for the increased sludge generation.

As shown in Figure 5.21, there was no discernable difference between the volume occupied by the sludge generated by the Denver cell and the volume occupied by the Wemco cell.

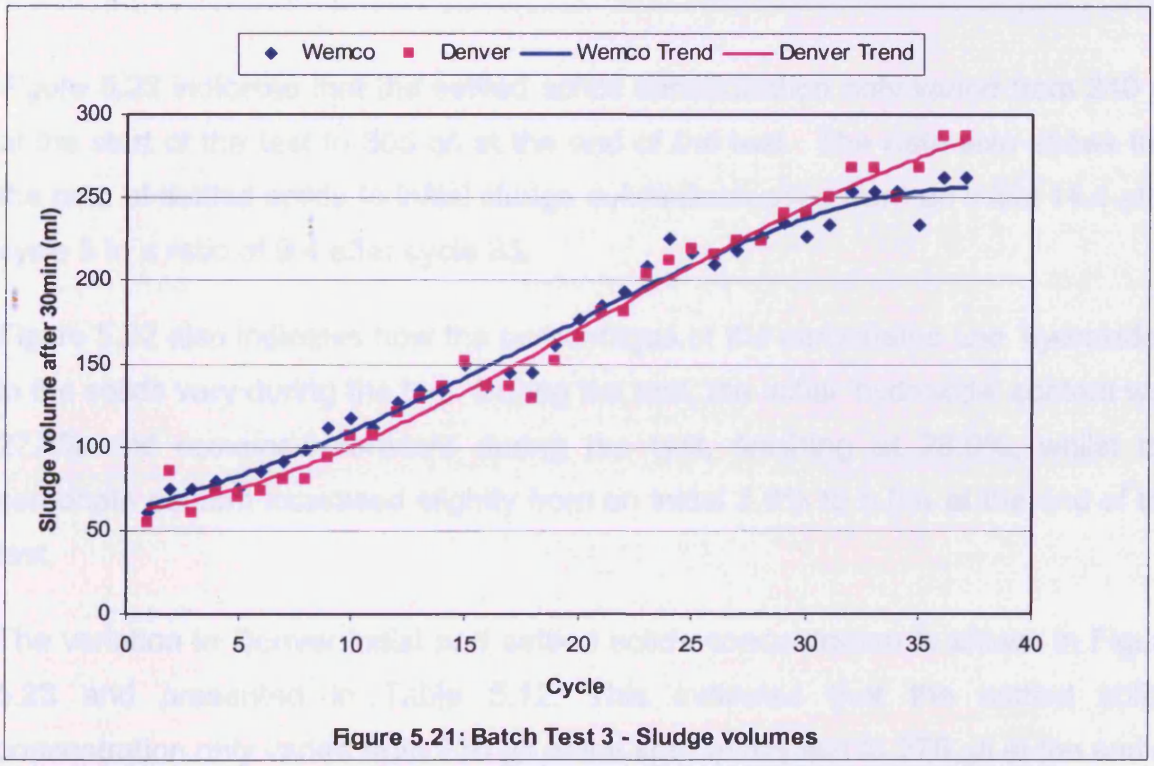


Figure 5.21: Batch Test 3 - Sludge volumes

5.8.2 Batch Test 3 – Sludge Composition

The variation in Wemco initial and settled sludge solids concentration after 30 minutes is shown in Figure 5.22 and presented in Table 5.11.

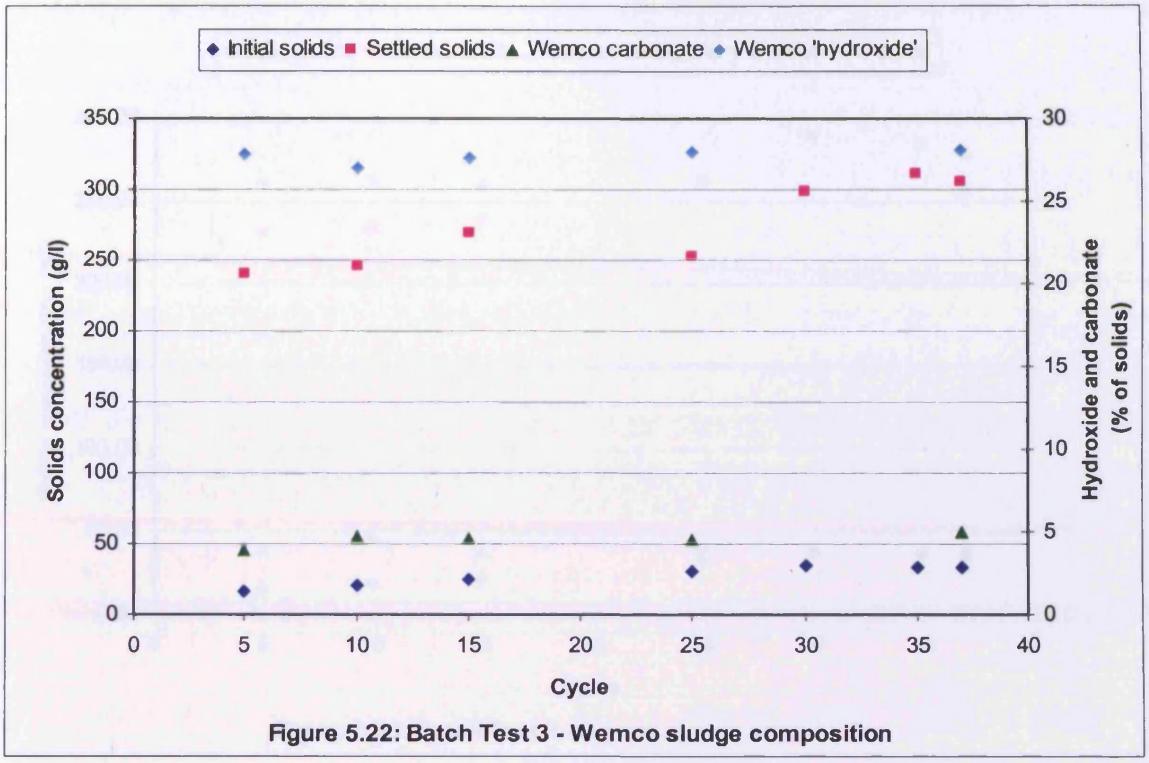


Figure 5.22: Batch Test 3 - Wemco sludge composition

Figure 5.22 indicates that the settled solids concentration only varied from 240 g/l at the start of the test to 305 g/l at the end of the test. The data also shows that the ratio of settled solids to initial sludge solids decreased from an initial 14.4 after cycle 5 to a ratio of 9.4 after cycle 35.

Figure 5.22 also indicates how the percentages of the carbonates and 'hydroxides' in the solids vary during the test. During the test, the initial 'hydroxide' content was 27.8% and remained constant during the test, finishing at 28.0%, whilst the carbonate content increased slightly from an initial 3.9% to 5.0% at the end of the test.

The variation in Denver initial and settled solids concentration is shown in Figure 5.23 and presented in Table 5.12. This indicates that the settled solids concentration only varied from 230 g/l at the start of the test to 278 g/l at the end of the test. The data also shows that the ratio of settled solids to initial sludge solids decreased from an initial 15.4 after cycle 5, to a ratio of 8.1 after cycle 35.

Figure 5.23 also indicates how the percentages of the carbonates and 'hydroxides' in the solids vary during the test. During the test, the 'hydroxide' content changed from an initial 26.0% to 25.7% at the end of the test, whilst the carbonate content increased from an initial 3.9% to 4.0% at the end of the test.

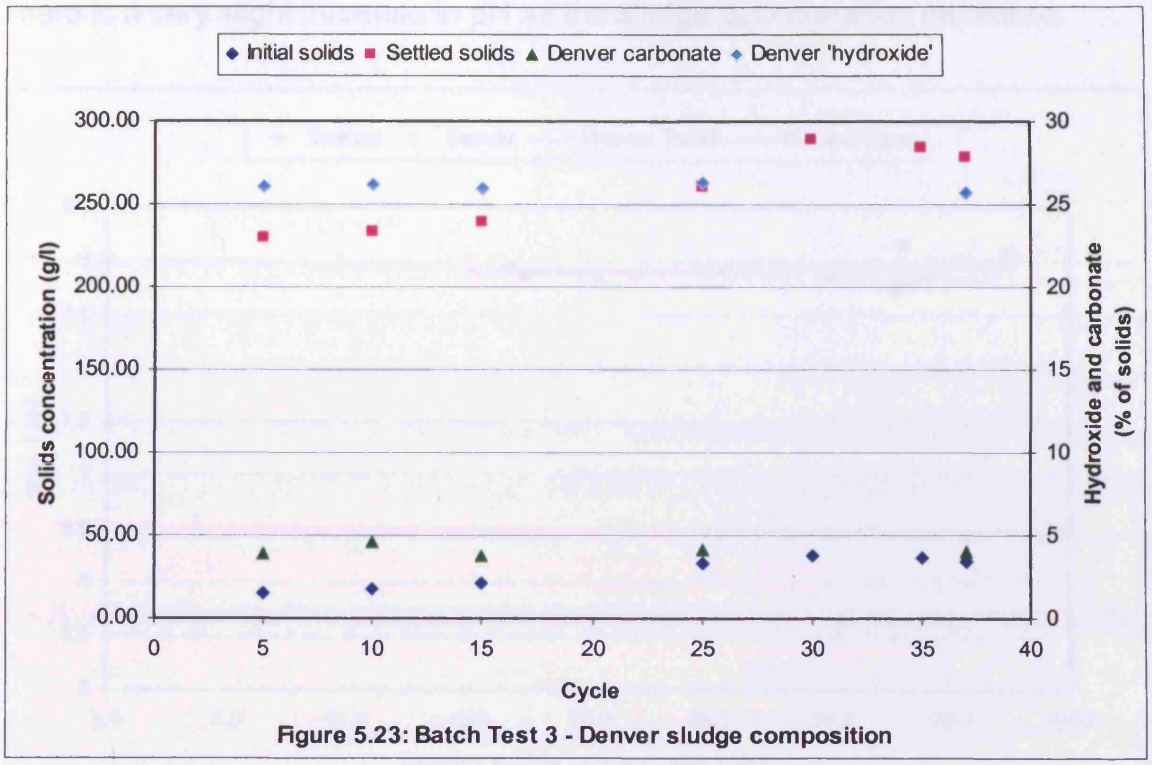


Figure 5.23: Batch Test 3 - Denver sludge composition

5.8.3 Batch Test 3 – pH Readings

The Step 1 pH readings for Batch Test 3 are presented in Figure 5.24. With the exception of the first readings, these show that throughout the test the Step 1 pHs for both the Wemco and the Denver cells remained constant at approximately 8.9.

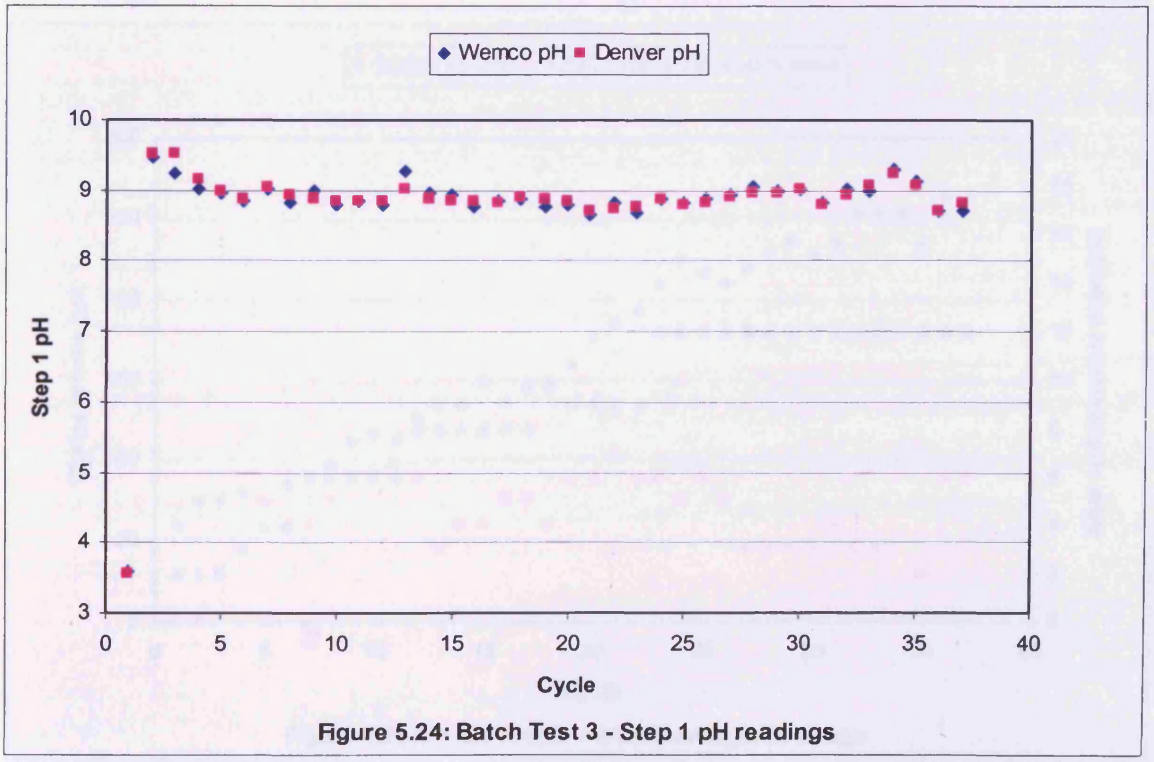


Figure 5.24: Batch Test 3 - Step 1 pH readings

Figure 5.25 shows how the initial pH varies with the reactor solids concentration.

There is a very slight increase in pH as the sludge concentration increases.

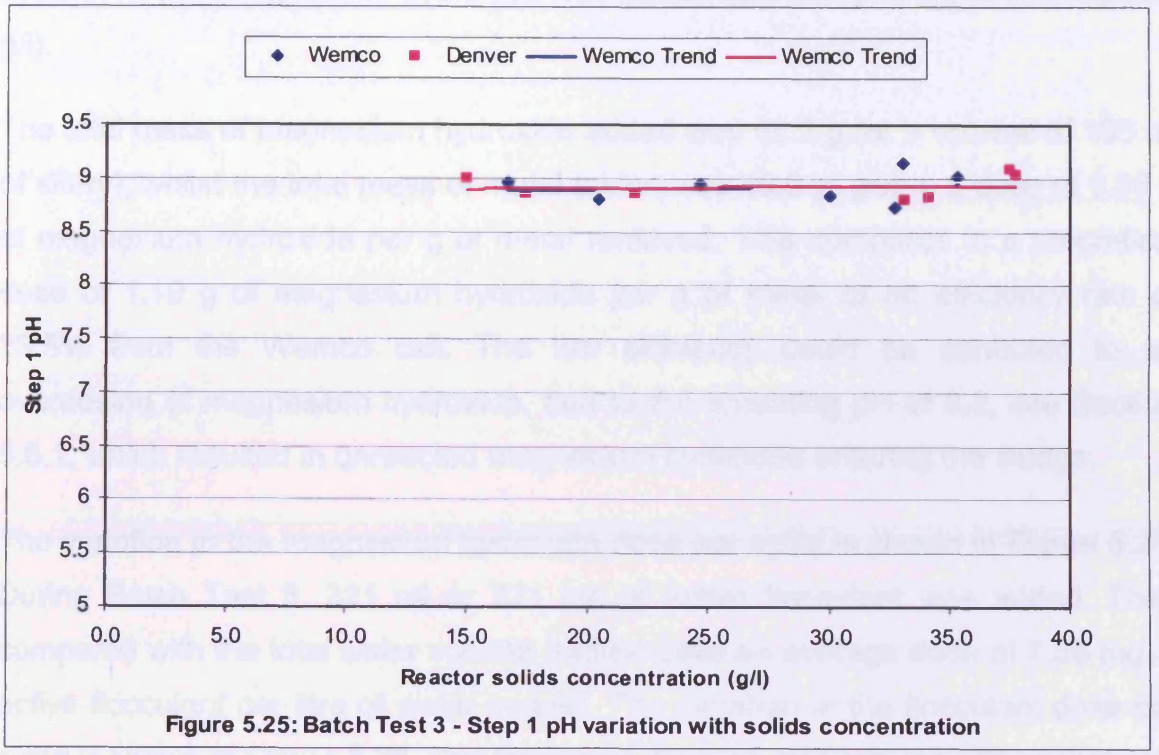


Figure 5.25: Batch Test 3 - Step 1 pH variation with solids concentration

5.8.4 Batch Test 3 – Reagent Use

The variations in the reagents used per cycle for the Wemco test are presented in Figure 5.26.

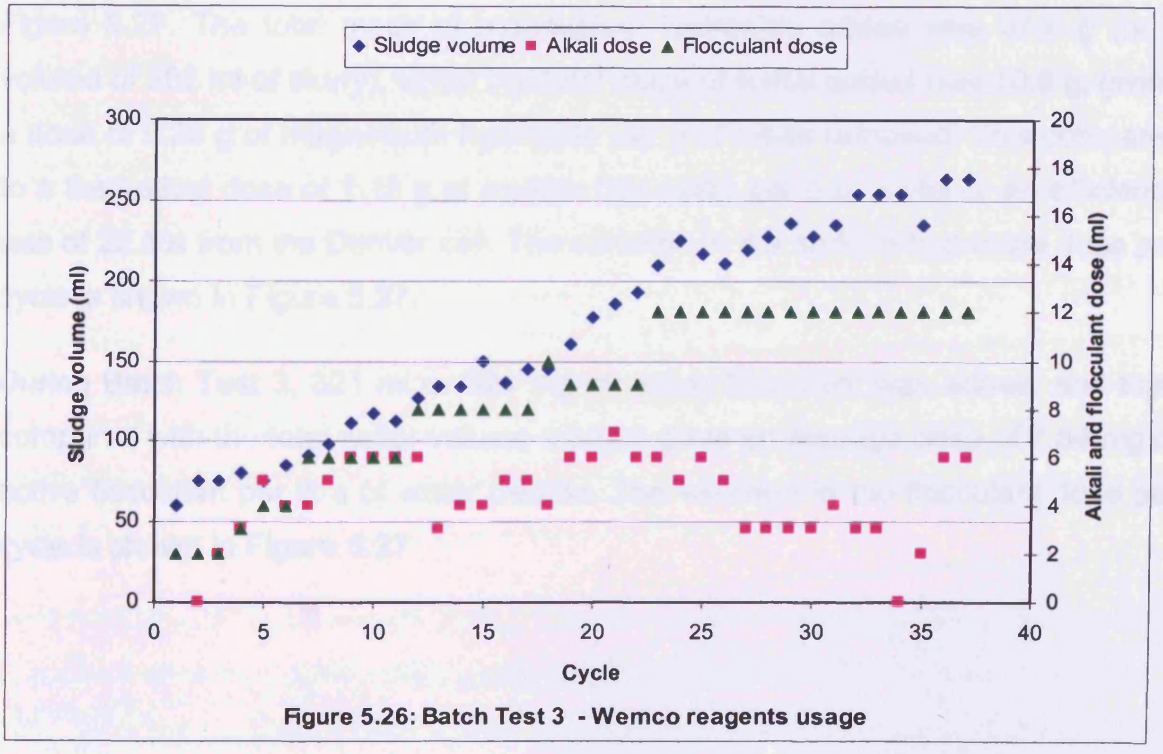


Figure 5.26: Batch Test 3 - Wemco reagents usage

The amount of alkali reagent, magnesium hydroxide, added was recorded per cycle in ml (the magnesium hydroxide was added as a slurry at approximately 286 g/l).

The total mass of magnesium hydroxide added was 55.2 g (or a volume of 193 ml of slurry), whilst the total mass of metal added was 10.9 g, giving a dose of 5.06 g of magnesium hydroxide per g of metal removed. This compares to a theoretical dose of 1.19 g of magnesium hydroxide per g of metal or an efficiency rate of 23.5% from the Wemco cell. The low efficiency could be attributed to an overdosing of magnesium hydroxide, due to the operating pH of 9.2, see Section 5.8.1, which resulted in unreacted magnesium hydroxide entering the sludge.

The variation in the magnesium hydroxide dose per cycle is shown in Figure 5.26. During Batch Test 3, 321 ml or 321 mg of active flocculant was added. That, compared with the total water volume treated gave an average dose of 7.86 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.26. The increased demand for flocculant (flocculant was added to maintain a clear supernatant liquid) as the test proceeded was likely to have been caused by the gradual increase in the reactor solids concentration as the test continued.

The variations in the reagents used per cycle for the Denver test are presented in Figure 5.27. The total mass of magnesium hydroxide added was 57.8 g (or a volume of 202 ml of slurry), whilst the total mass of metal added was 10.9 g, giving a dose of 5.29 g of magnesium hydroxide per g of metal removed. This compares to a theoretical dose of 1.19 g of sodium hydroxide per g of metal or an efficiency rate of 22.5% from the Denver cell. The variation in the sodium hydroxide dose per cycle is shown in Figure 5.27.

During Batch Test 3, 321 ml or 321 mg of active flocculant was added, and that, compared with the total water volume treated, gave an average dose of 7.84 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.27.

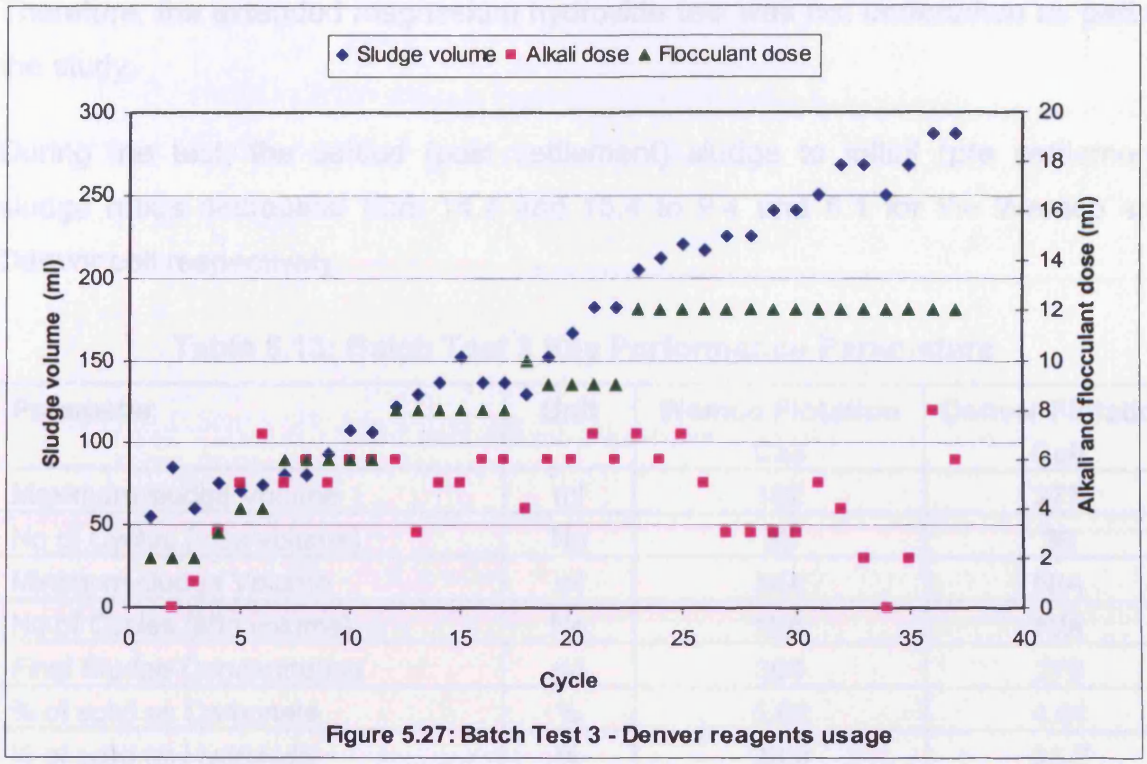


Figure 5.27: Batch Test 3 - Denver reagents usage

5.8.5 Batch Test 3 – Summary of Key Performance Parameters

The key performance indicators of Batch Test 3 are presented in Table 5.13.

During Batch Test 3, the sludge volumes did not reduce in volume as the test progressed. It is therefore concluded that either more cycles would be required to produce HDS sludge when using magnesium hydroxide as the alkali reagent, or HDS cannot be formed when using magnesium hydroxide. A test of approximately 100 cycles would be required to confirm if HDS sludge could be produced when using magnesium hydroxide as the alkali reagent. This number of cycles was estimated by comparing Figures 5.19 and 5.20 with Figure 5.1, where it is suggested that the height of the sludge volumes in Figure 5.19 and 5.20, where the sludge volumes appear to have 'plateauxed', equates to point C on Figure 5.1.

The results of the work undertaken would suggest that the presence of other elements, such as calcium and magnesium, can 'swamp' the HDS process and slow down the formation of HDS sludge, see Chapter 8.

As it had already been shown during Batch Test 1 and 2 that HDS sludge could be produced after 35 cycles when using sodium hydroxide and calcium hydroxide, it was considered that it would not be commercially viable to use magnesium hydroxide as the alkali reagent on a full-scale minewater treatment plant.

Therefore, the extended magnesium hydroxide test was not undertaken as part of the study.

During the test, the settled (post settlement) sludge to initial (pre settlement) sludge ratios decreased from 14.4 and 15.4 to 9.4 and 8.1 for the Wemco and Denver cell respectively.

Table 5.13: Batch Test 3 Key Performance Parameters

Parameter	Unit	Wemco Flotation Cell	Denver Flotation Cell
Maximum sludge Volume	ml	162	277
No of Cycles (max volume)	No	36	36
Minimum sludge Volume	ml	N/A	N/A
No of Cycles (Min volume)	No	N/A	N/A
Final Sludge Concentration	g/l	305	278
% of solid as Carbonate	%	5.02	4.01
% of solid as Hydroxide	%	28.0	25.7
Flocculant dose	mg/l	7.86	7.84
Stage I pH	pH unit	8.9	8.9
Stage II pH	pH unit	9.43	9.41
Alkali used (magnesium hydroxide)	ml	193	202
Alkali usage (magnesium hydroxide)	mg/l	1490	1560
Alkali efficiency	%	23.5	22.5
Total feed metal concentration	mg/l	310	310
Total feed metal hydroxide	mg/l	592	592
Sludge generation: Measured generation Calculated generation (from sludge composition)	 mg/l mg/l	 2160 1610	 2160 1690
Sludge concentration ratios (Settled/Initial) Cycle 5 Cycle 35	 Ratio Ratio	 14.4 9.4	 15.4 8.1

5.9 Batch Test 4 – Synthetic Wheal Jane Minewater Treated with Sodium Carbonate

During Batch Test 4, 30 cycles were undertaken with the feed water and treated water quality as presented in Table 5.14. The pH of the feed water of 1.4 and 1.3 and the pH of the treated water of 1.5 was due to the waters being acidified with hydrochloric acid prior to analysis. The difference in the feed and treated water sulphate was likely to have been due to the precipitation of some of the sulphate

during the batch test.

Table 5.14: Batch Test 4 Water Quality Summary

Sample	pH	Solids mg/l	Fe mg/l	SO_4 mg/l	Ca mg/l	Zn Mg/l	Al mg/l
Feed water	1.4	<1	216	840	<1	56	38
Feed water	1.3	<1	225	811	<1	59	40
Treated water	1.5	<1	15	659	<1	3.7	5.3

5.9.1 Batch Test 4 – Sludge Volume and Sludge Mass

Presented in Figure 5.28 is how the mass and volume of the sludge in the system varied with the number of cycles for the Wemco flotation cell. The sludge concentrations are presented in Table 5.15 along with the supernatant and initial solids concentrations.

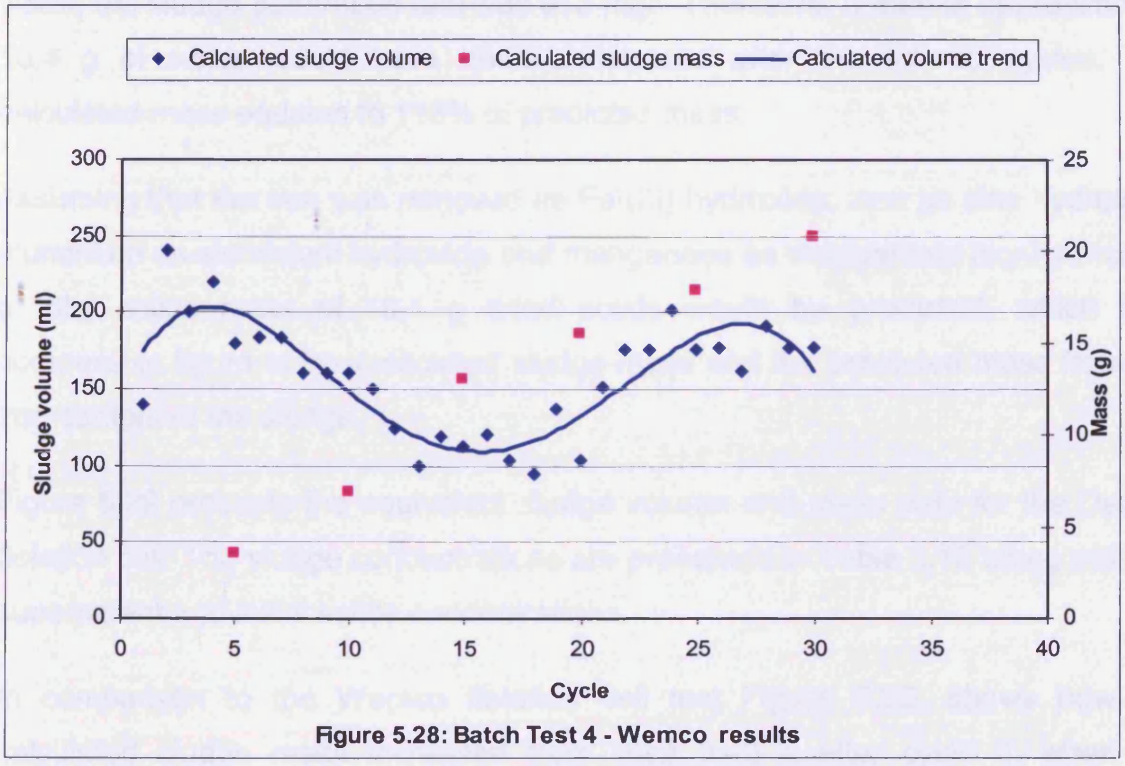


Figure 5.28: Batch Test 4 - Wemco results

Table 5.15: Batch Test 4 Wemco sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 20	Cycle 25	Cycle 30
Initial solids	g/l	2.69	5.28	9.53	8.37	6.57	6.66
Sludge solids	g/l	18.3	43.0	116	151	101	118
Supernatant solids	mg/l	55	33	123	201	104	89

Figure 5.28 shows how the calculated sludge mass increased from circa 3.55 g

after cycle 5, when the calculated sludge volume was 180 ml, to 20.8 g after cycle 30. During this period the calculated sludge volume had decreased to approximately 177 ml.

As with Batch Test 1, the calculated sludge volume trend line (5^{th} order polynomial) presented in Figure 5.28 was generated by the Excel spreadsheet package; this resulted the peak in the trend line after cycle 25.

The total mass of solids generated during the test was 20.8 g of dried solids, or a solids generation rate of 693 mg of solids per litre of minewater treated.

Analysis of the final sludge generated during the test indicated that 36.0% of the solid was iron, 6.3% was zinc and 3.5% was aluminium. Using the iron solid percentage of 36.0%, a solids generation rate of 2.78 g of sludge per g of iron removed was calculated. Using an iron concentration of 221 mg/l in the feed water, the sludge generation rate was 613 mg/l. Therefore, a total of approximately 18.4 g of solids would have been anticipated after the full 30 cycles. The calculated mass equates to 113% of predicted mass.

Assuming that the iron was removed as Fe (III) hydroxide, zinc as zinc hydroxide, aluminium as aluminium hydroxide and manganese as manganese oxy-hydroxide, a total solids mass of 19.1 g dried solids would be predicted, which is a comparable figure to the calculated sludge mass and the predicted mass from the iron content of the sludge.

Figure 5.29 presents the equivalent sludge volume and mass data for the Denver flotation cell. The sludge concentrations are presented in Table 5.16 along with the supernatant and initial solids concentrations.

In comparison to the Wemco flotation cell test Figure 5.29, shows how the calculated sludge mass increased from circa 3.43 g after cycle 5, when the calculated sludge volume was 210 ml, to 15.7 g after cycle 30. During this period the calculated sludge volume had decreased to approximately 153 ml.

The total mass of solids generated during the test was 15.7 g of dried solids or a solids generation rate of 524 mg of solids per litre of minewater treated. This indicates that the Wemco unit produced an extra 169 mg/l of solids per cycle, which is equivalent to 32% increase in the sludge production rate.

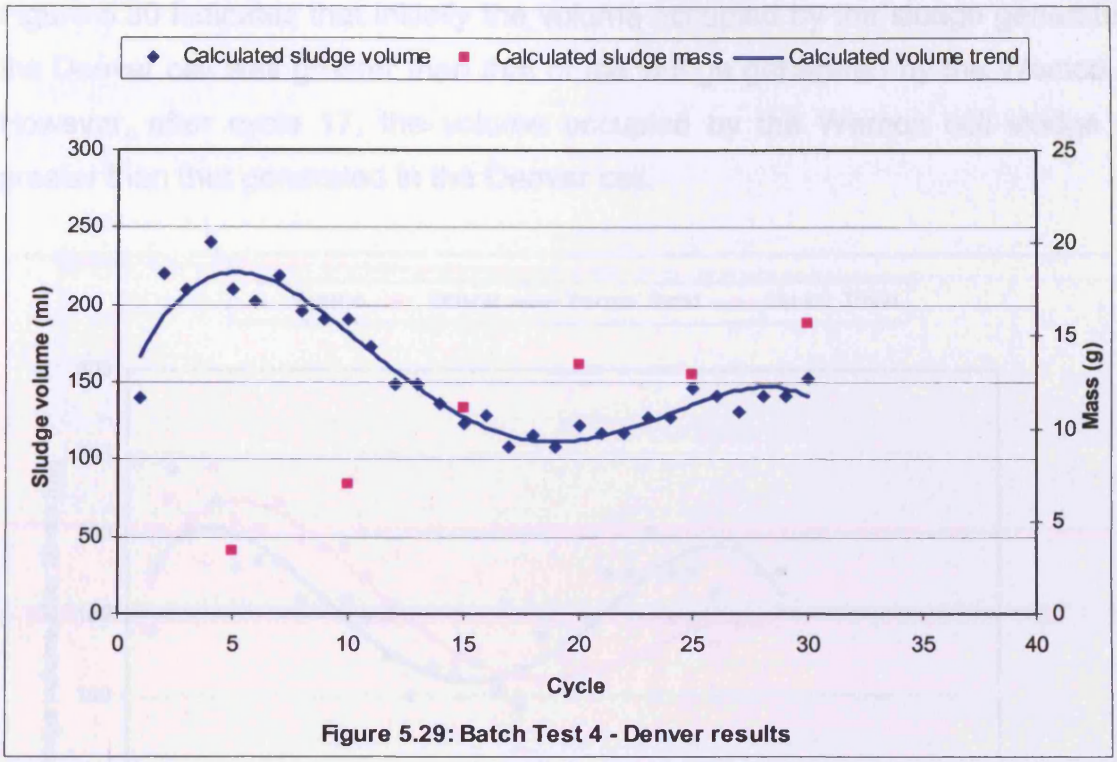


Figure 5.29: Batch Test 4 - Denver results

Table 5.16: Batch Test 4 Denver sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 20	Cycle 25	Cycle 30
Initial solids	g/l	2.59	5.33	8.09	9.17	6.24	6.78
Sludge solids	g/l	15.3	36.7	89.8	110	88.7	103
Supernatant solids	mg/l	44	33	85	154	110	4

Analysis of the final sludge generated during the test indicated that 37.6% of the solid was iron, 8.6% was zinc and 3.9% was aluminium. Using the iron solid percentage of 37.6%, a solids generation rate of 2.66 g of sludge per g of iron removed was calculated. Using an iron concentration of 221 mg/l in the feed water, the sludge generation rate was 586 mg/l. Therefore, a total of approximately 17.6 g of solids would have been anticipated by the end of cycle 30. The calculated mass equates to 89% of predicted mass.

Assuming that the iron was removed as Fe (III) hydroxide, zinc as zinc hydroxide, aluminium as aluminium hydroxide and manganese as manganese oxy-hydroxide, a total solids mass of 19.1 g dried solids would be predicted, which is a comparable figure to the calculated sludge mass and the predicted mass from the iron content of the sludge.

Figure 5.30 indicates that initially the volume occupied by the sludge generated in the Denver cell was greater than that of the sludge generated by the Wemco cell. However, after cycle 17, the volume occupied by the Wemco cell sludge was greater than that generated in the Denver cell.

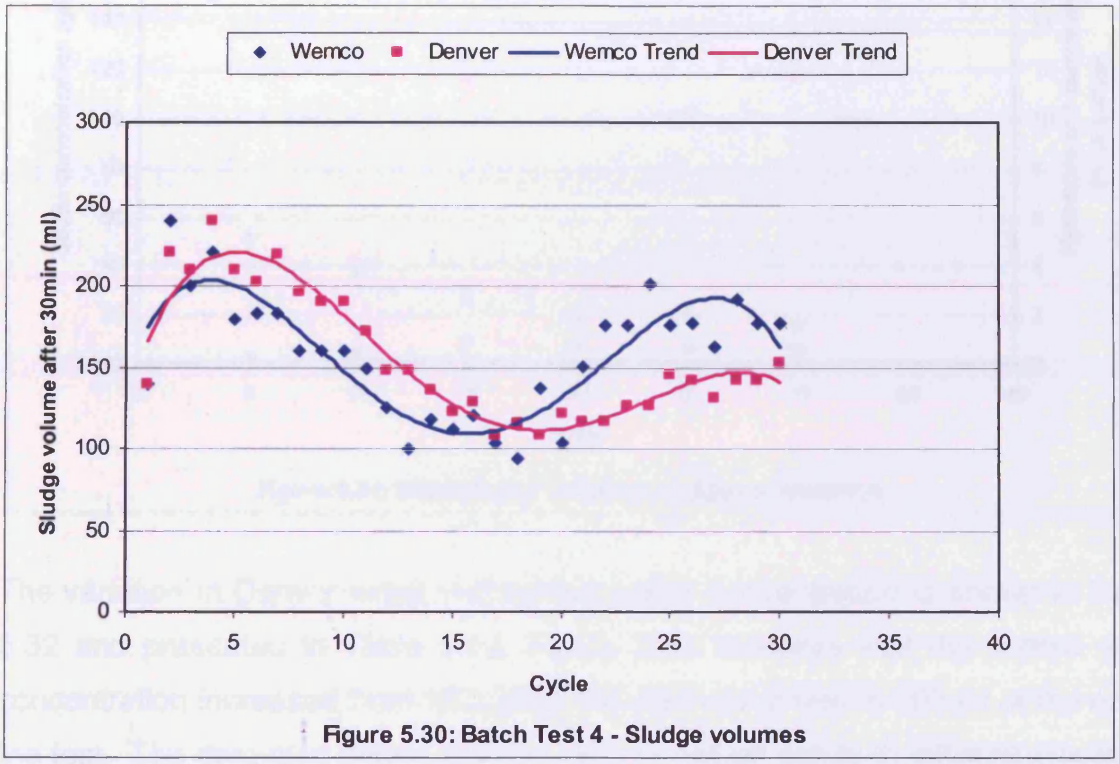


Figure 5.30: Batch Test 4 - Sludge volumes

5.9.2 Batch Test 4 – Sludge Composition

The variation in Wemco initial and settled sludge solids concentration after 30 minutes is shown in Figure 5.31 and presented in Table 5.15. This indicates that the settled solids concentration increased from 18.3 g/l after cycle 5 to 118 g/l after cycle 30. The data also shows that the ratio of settled solids to initial sludge solids decreased from an initial 6.8 after cycle 5 to a ratio of 17.7 after cycle 30. It is worth noting though sodium carbonate was used as the alkali reagent the iron was still removed as iron hydroxides (see Section 2.6.2).

Figure 5.31 also demonstrates how the percentages of the carbonates and 'hydroxides' in the solids vary during the test. During the test, the initial 'hydroxide' content was 17.0% and increased slightly to 19.0% by the end of the test, whilst the carbonate content decreased slightly from an initial 5.4% to 1.6% at the end of the test.

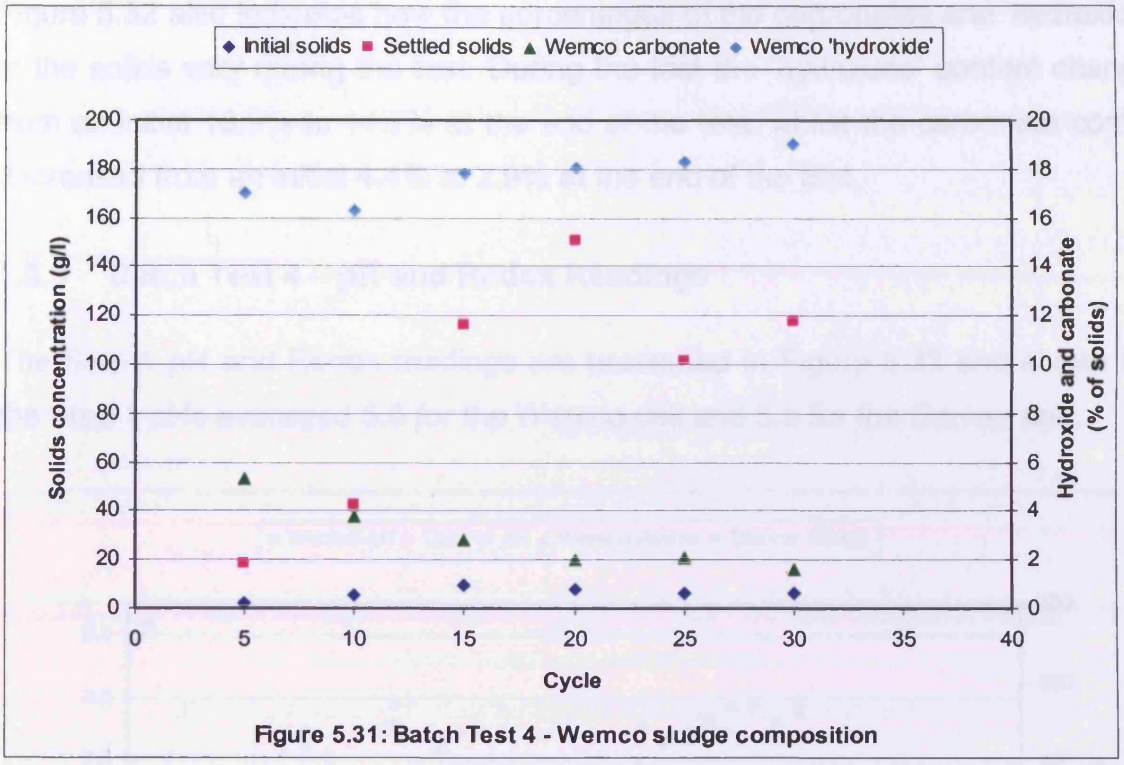


Figure 5.31: Batch Test 4 - Wemco sludge composition

The variation in Denver initial and settled solids concentration is shown in Figure 5.32 and presented in Table 5.16. Figure 5.32 indicates that the settled solids concentration increased from 15.3 g/l at the start of the test to 103 g/l at the end of the test. The data also shows that the ratio of settled solids to initial sludge solids increased from an initial 5.9 after cycle 5 to a ratio of 15.2 after cycle 30.

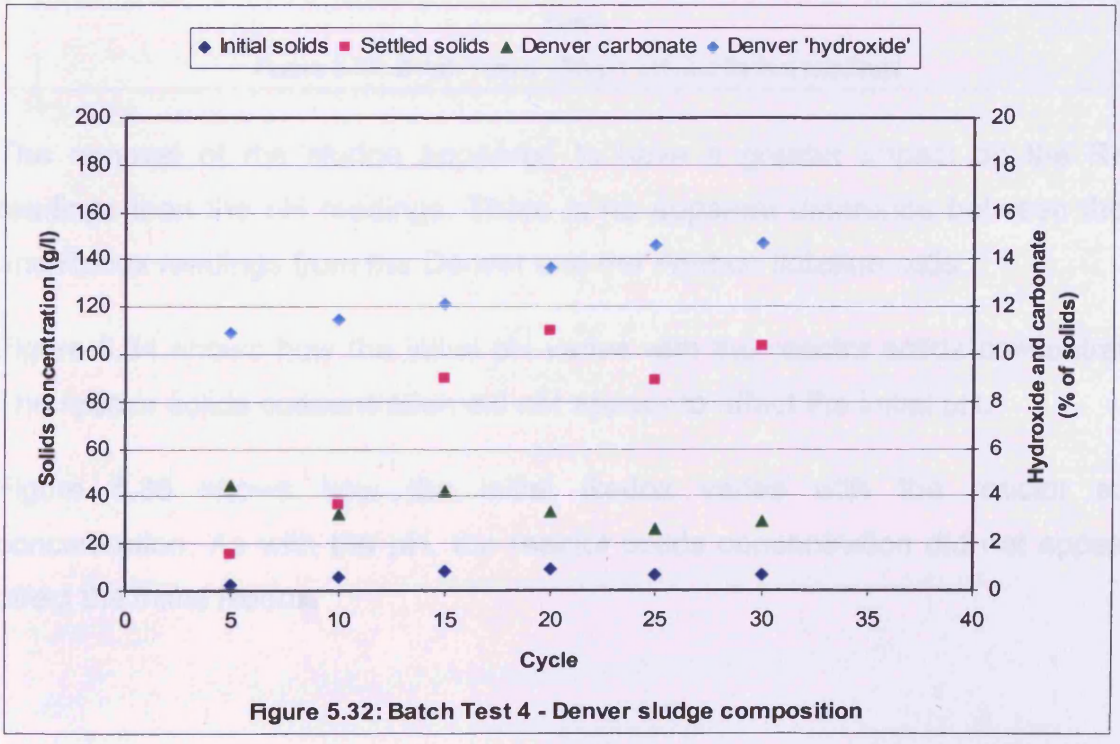


Figure 5.32: Batch Test 4 - Denver sludge composition

Figure 5.32 also indicates how the percentages of the carbonates and 'hydroxides' in the solids vary during the test. During the test the 'hydroxide' content changed from an initial 10.9% to 14.7% at the end of the test, whilst the carbonate content decreased from an initial 4.4% to 2.9% at the end of the test.

5.9.3 Batch Test 4 – pH and Redox Readings

The Step 1 pH and Redox readings are presented in Figure 5.33 and shows that the Step 1 pHs averaged 5.5 for the Wemco cell and 5.9 for the Denver cell.

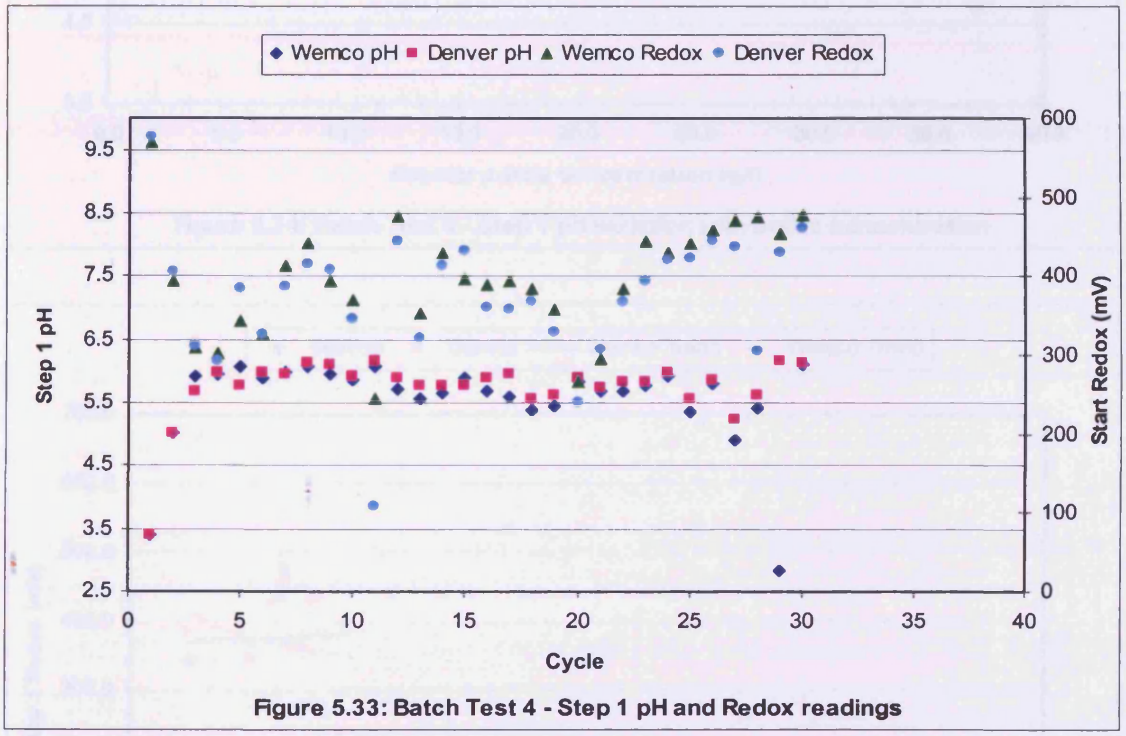


Figure 5.33: Batch Test 4 - Step 1 pH and Redox readings

The removal of the sludge appeared to have a greater impact on the Redox readings than the pH readings. There is no apparent difference between the pH and Redox readings from the Denver and the Wemco flotation cells.

Figure 5.34 shows how the initial pH varies with the reactor solids concentration. The reactor solids concentration did not appear to affect the initial pH.

Figure 5.35 shows how the initial Redox varies with the reactor solids concentration. As with the pH, the reactor solids concentration did not appear to affect the initial Redox.

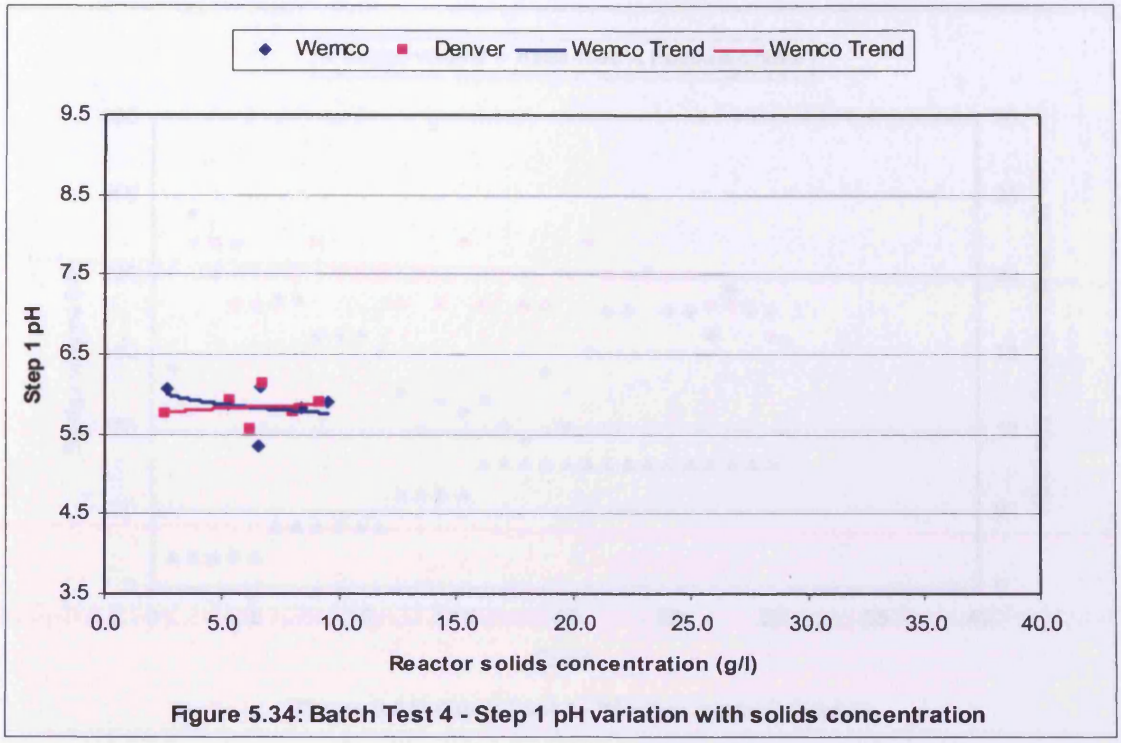


Figure 5.34: Batch Test 4 - Step 1 pH variation with solids concentration

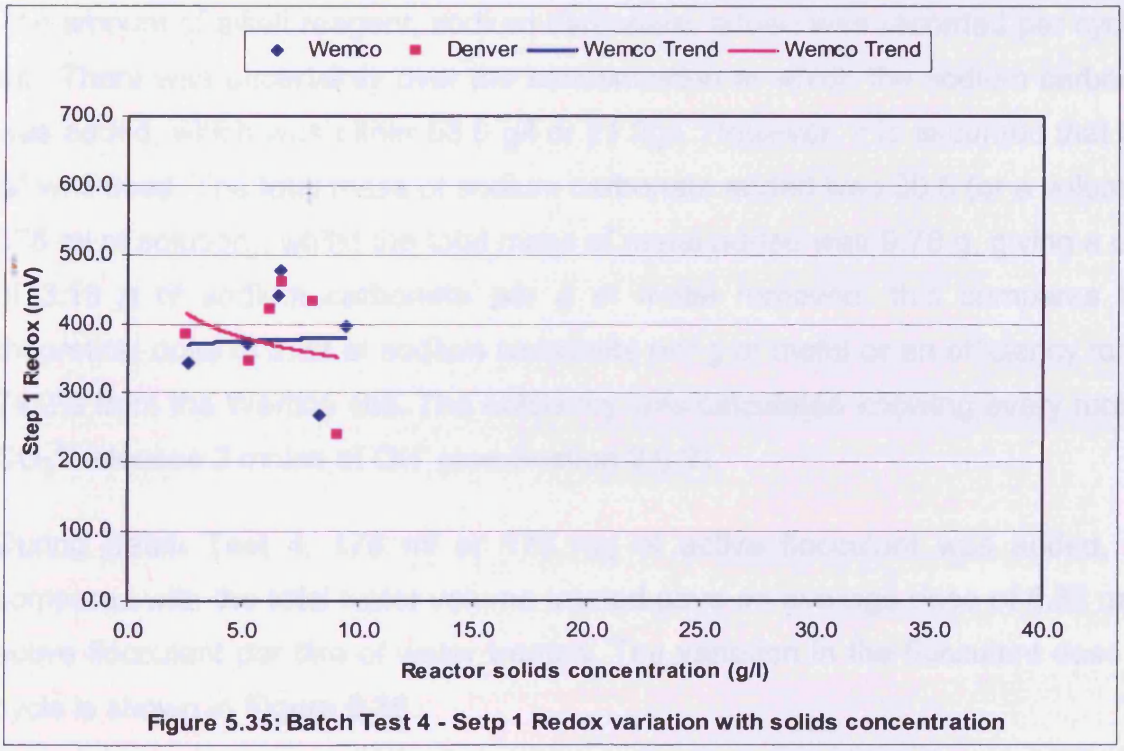


Figure 5.35: Batch Test 4 - Setp 1 Redox variation with solids concentration

5.9.4 Batch Test 4 – Reagent Use

The variations in the reagents used per cycle for the Wemco Test are presented in Figure 5.36.

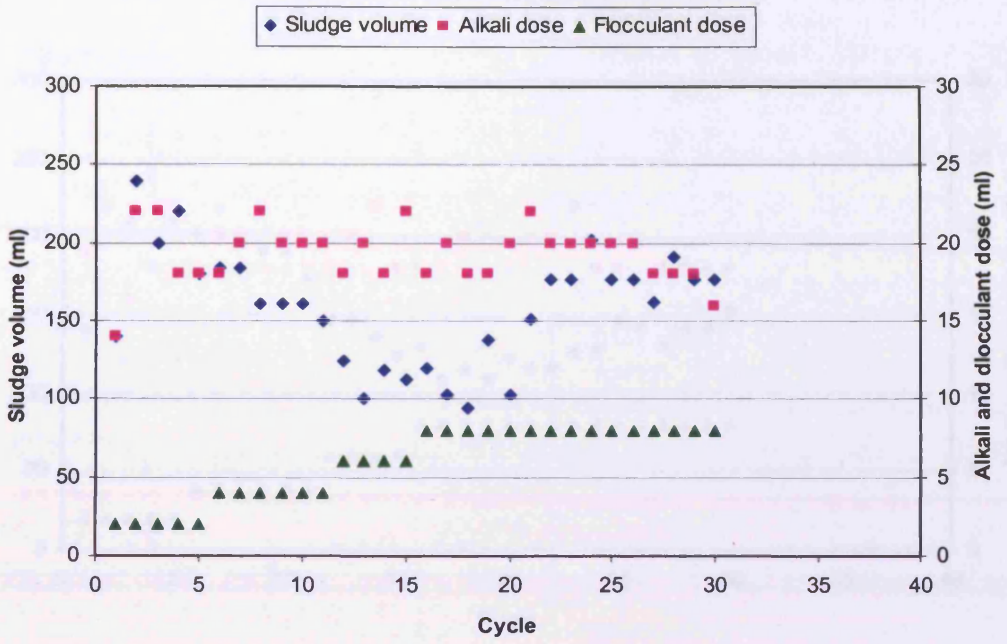


Figure 5.36: Batch Test 4 - Wemco reagents usage

The amount of alkali reagent, sodium carbonate, added was recorded per cycle in ml. There was uncertainty over the concentration at which the sodium carbonate was added, which was either 53.0 g/l or 21.2g/l. However, it is assumed that 53.0 g/l was used. The total mass of sodium carbonate added was 30.6 (or a volume of 578 ml of solution), whilst the total mass of metal added was 9.78 g, giving a dose of 3.13 g of sodium carbonate per g of metal removed, this compares to a theoretical dose of 2.32 of sodium carbonate per g of metal or an efficiency rate of 74.2% from the Wemco cell. The efficiency was calculated knowing every mole of CO_3^{2-} releases 2 moles of OH^- (see Section 2.6.2).

During Batch Test 4, 178 ml or 178 mg of active flocculant was added, and compared with the total water volume treated gave an average dose of 5.36 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.36.

The variations in the reagents used per cycle for the Denver Test are presented in Figure 5.37. The total mass of sodium carbonate added was 30.4 g (or a volume of 573 ml of solution), whilst the total mass of metal added was 9.78 g, which gave a dose of 3.10 g of sodium carbonate per g of metal removed. This compares to a theoretical dose of 2.32 g of sodium carbonate per g of metal or an efficiency rate of 75% from the Denver cell. The variation in the sodium carbonate dose per cycle is shown in Figure 5.37.

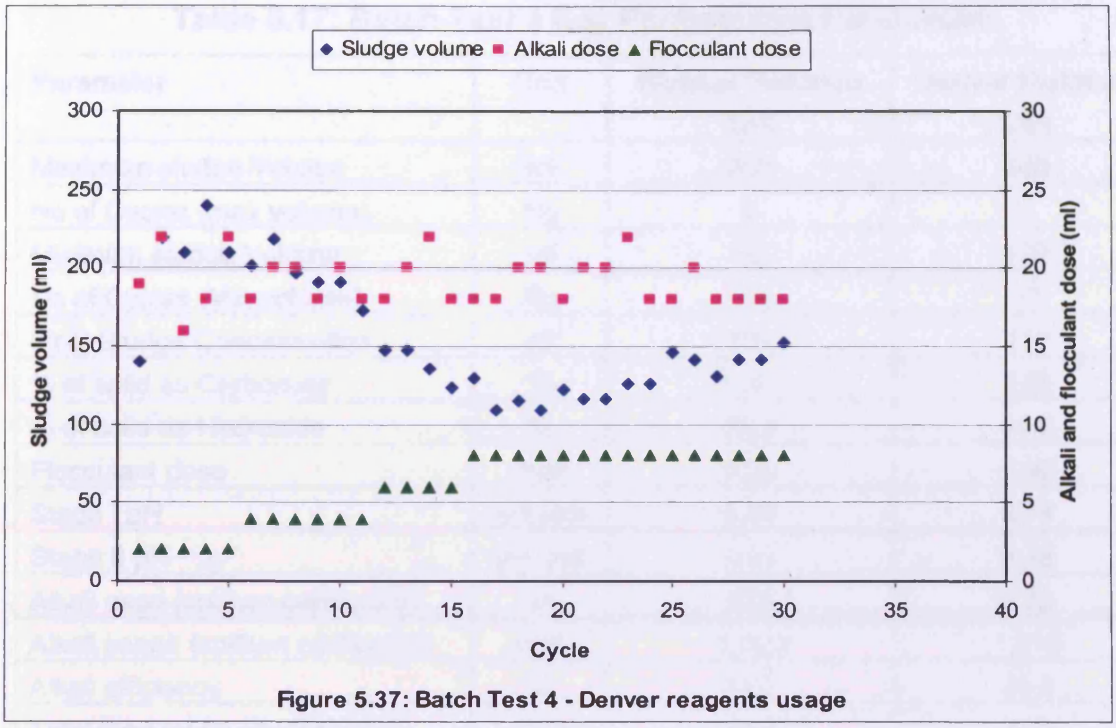


Figure 5.37: Batch Test 4 - Denver reagents usage

During Batch Test 4, 178 ml or 178 mg of active flocculant was added, and that compared with the total water volume treated gave an average dose of 5.30 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.37.

5.9.5 Batch Test 4 – Summary of Key Performance Parameters

The key performance indicators of Batch Test 4 are presented in Table 5.17. As with Batch Tests 1 and 2, the settling characteristics of the sludge generated in Batch Test 4 were similar to those of HDS sludge.

After cycle 35 of the Wemco test, the ratio of settled (post settlement) sludge concentration to initial (pre settlement) sludge concentration, and hence volumes, was 17.7 compared to a ratio of 6.8 after cycle 5.

The Denver settled (post settlement) sludge concentration to initial (pre settlement) sludge concentration after cycle 35 was 15.2, slightly lower than for the Wemco cell. Hence a less densely settling sludge was formed. As with previous batch tests, this was likely to have been caused by either; the extra shearing exerted on the sludge by the Wemco cell, or the higher carbonate composition in the sludge as a result of the increased air flow in the Denver cell compared to the Wemco cell.

Table 5.17: Batch Test 4 Key Performance Parameters

Parameter	Unit	Wemco Flotation Cell	Denver Flotation Cell
Maximum sludge Volume	ml	240	240
No of Cycles (max volume)	No	2	4
Minimum sludge Volume	ml	95	109
No of Cycles (Min volume)	No	18	17
Final Sludge Concentration	g/l	151	110
% of solid as Carbonate	%	1.42	2.88
% of solid as Hydroxide	%	22.4	14.7
Flocculant dose	mg/l	5.36	5.30
Stage I pH	pH unit	5.34	5.74
Stage II pH	pH unit	9.24	9.28
Alkali used (sodium carbonate)	ml	578	5.73
Alkali usage (sodium carbonate)	mg/l	1,020	1,010
Alkali efficiency	%	74.2	75.0
Total feed metal concentration	mg/l	310	310
Total feed metal hydroxide	mg/l	592	592
Sludge generation: Measured generation Calculated generation (from sludge composition)	 mg/l mg/l	 693 613	 524 586
Sludge concentration ratios (Settled/Initial) Cycle 5 Cycle 35	 Ratio Ratio	 6.8 17.7	 5.9 15.2

5.10 Batch Tests 5 and 6 – Synthetic Zinc and Aluminium Minewater Treated with Calcium Hydroxide

During Batch Tests 5 and 6, 20 cycles were undertaken with the feed water and treated water as presented in Table 5.18.

Table 5.18: Batch Tests 5 and 6 Water Quality Summary

Sample	pH	Solids mg/l	Fe Mg/l	SO_4 mg/l	Ca mg/l	Zn mg/l	Al mg/l
Feed water	1.4	50	-	15,600	<1	186	-
Feed water	1.4	120	-	21,300	<1	-	155
Treated water	1.4	74	-	18,300	69	3.8	-
Treated water	1.4	102	-	18,500	<1	-	14

In Batch Test 5, synthetic zinc minewater was treated with calcium hydroxide, whilst in Batch Test 6, calcium hydroxide was used to treat synthetic aluminium

minewater. The Wemco flotation cell was used for Batch Test 5 and the Denver was used during Batch Test 6.

5.10.1 Batch Tests 5 and 6 – Sludge Volume and Sludge Mass

Presented in Figure 5.38 is how the sludge volume varied with the number of cycles for the synthetic zinc minewater (the Wemco flotation cell). The sludge concentrations are presented in Table 5.19 along with the supernatant and initial solids concentrations.

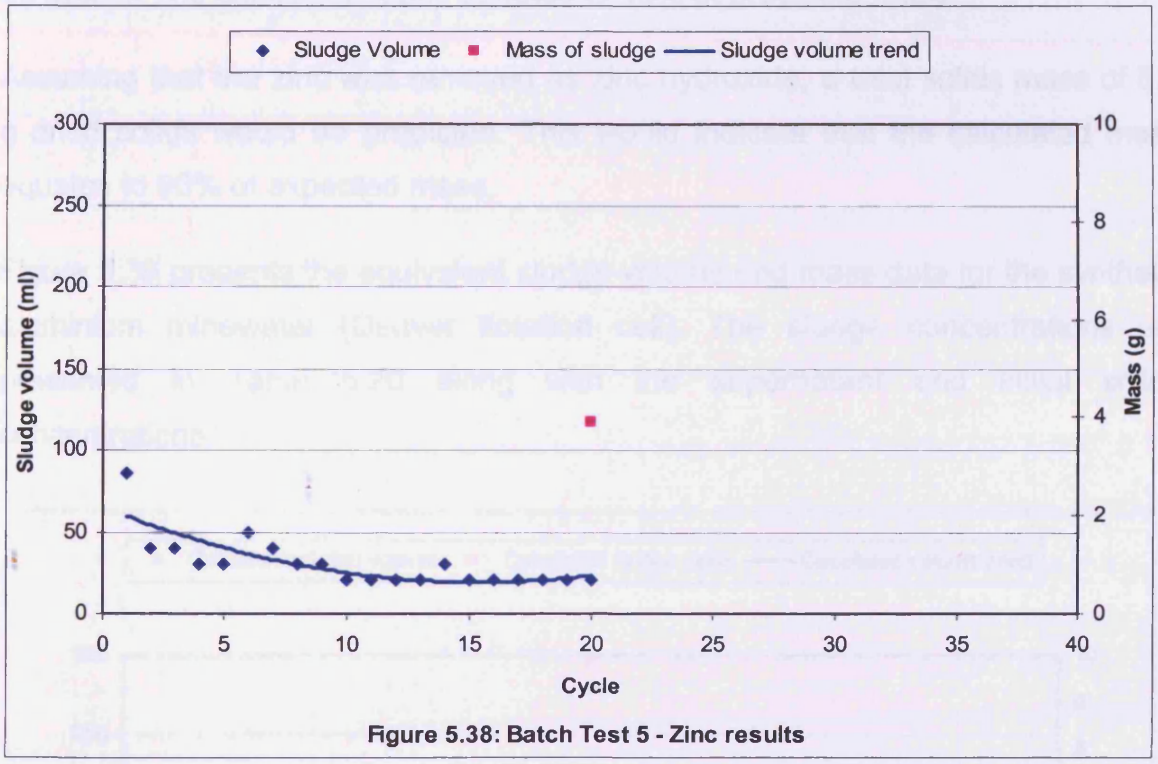


Figure 5.38: Batch Test 5 - Zinc results

Table 5.19: Batch Test 5 Sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 20
Initial solids	g/l	-	-	-	3.84
Sludge solids	g/l	-	-	-	196
Supernatant solids	mg/l	12	2	11	0

Due to low sludge generation, it was not possible to remove sludge during Batch Test 5 (synthetic zinc test), therefore sludge analysis was only undertaken at the end of the test, after cycle 20. Figure 5.38 shows how the sludge volume only varied slightly during the test. At the end of the test, the sludge mass was 5.04 g, when the calculated sludge volume was 20 ml. A small amount, approximately 1 g, of solids was lost accidentally from the reactor after cycle 7. The total mass of solids generated during the test was 5.04 g of dried solids, or a solids generation

rate of 252 mg of solids per litre of minewater treated.

Analysis of the final sludge generated during the test indicated that 35.3% of the solid was zinc, 0.5% was iron and 0.08% was aluminium. It is assumed that the other metals present were present due to contamination from the flotation cell. Using the zinc solid percentage of 35.3%, a solids generation rate of 2.83 g of sludge per g of zinc removed was calculated. Using a zinc concentration of 186mg/l in the feed water, the sludge generation rate was 527 mg/l. Therefore, a total of approximately 10,500 g of solids would have been anticipated after the full 20 cycles. The calculated mass equates to 48% of predicted mass.

Assuming that the zinc was removed as zinc hydroxide, a total solids mass of 5.6 g dried solids would be predicted. This would indicate that the calculated mass equates to 90% of expected mass.

Figure 5.39 presents the equivalent sludge volume and mass data for the synthetic aluminium minewater (Denver flotation cell). The sludge concentrations are presented in Table 5.20 along with the supernatant and initial solids concentrations.

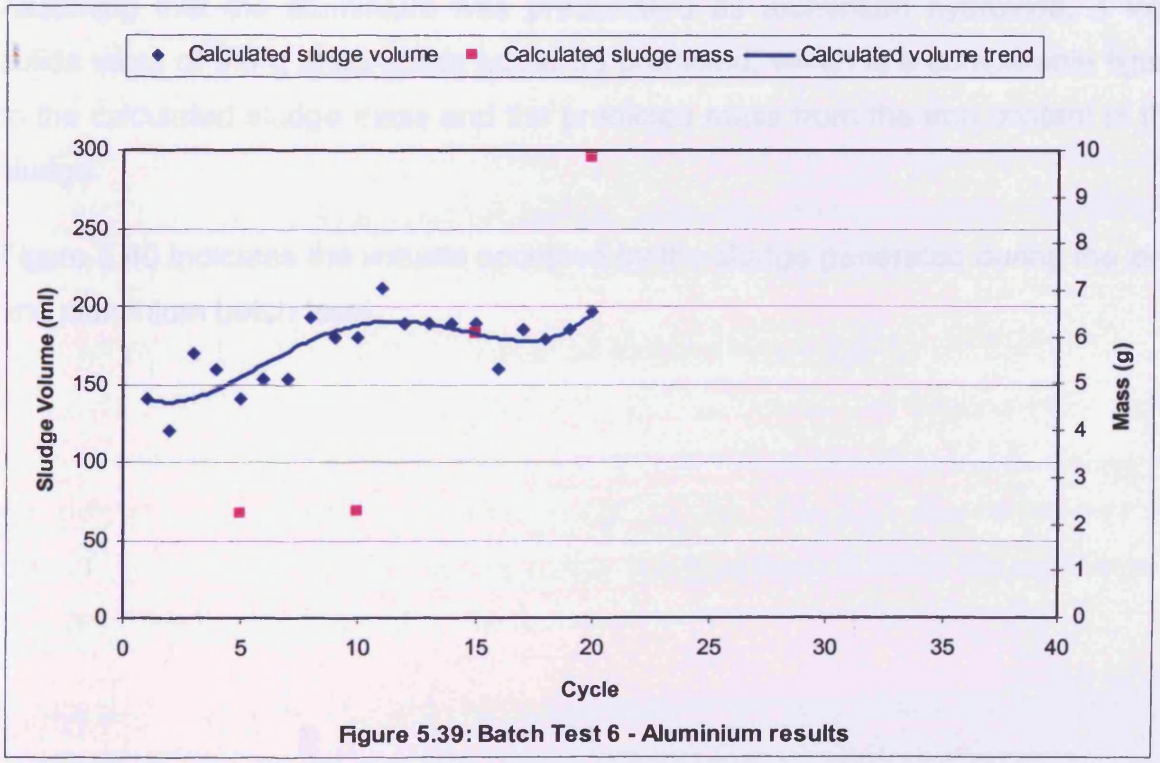


Figure 5.39: Batch Test 6 - Aluminium results

In comparison to the synthetic zinc minewater test, Figure 5.40 shows how the calculated sludge mass increased from circa 2.24 g after cycle 5, when the

calculated sludge volume was 149 ml, to 9.83 g after cycle 20. During this period, the calculated sludge volume had increased to approximately 196 ml.

Table 5.20: Batch Test 6 Sludge and supernatant solids concentrations

Sample	Unit	Cycle 5	Cycle 10	Cycle 15	Cycle 20
Initial solids	g/l	1.89	1.57	4.45	6.96
Sludge solids	g/l	15.6	12.8	32.3	50.0
Supernatant solids	mg/l	10	12	17	23

The total mass of solids generated during the test was 9.83 g of dried solids or a solids generation rate of 452 mg of solids per litre of minewater treated.

Analysis of the final sludge generated during the test indicated that 0.9% of the solid was iron, 0.6% was zinc and 24.8% was aluminium. Using the aluminium solid percentage of 24.8%, a solids generation rate of 4.04 g of sludge per g of aluminium removed was calculated. Using an aluminium concentration of 155 mg/l in the feed water, the sludge generation rate was 626mg/l. Therefore, a total of approximately 12,500 g of solids would have been anticipated by the end of cycle 20. The calculated mass equates to 79% of predicted mass.

Assuming that the aluminium was precipitated as aluminium hydroxide, a total solids mass of 9.0 g dried solids would be predicted, which is a comparable figure to the calculated sludge mass and the predicted mass from the iron content of the sludge.

Figure 5.40 indicates the volume occupied by the sludge generated during the zinc and aluminium batch tests.

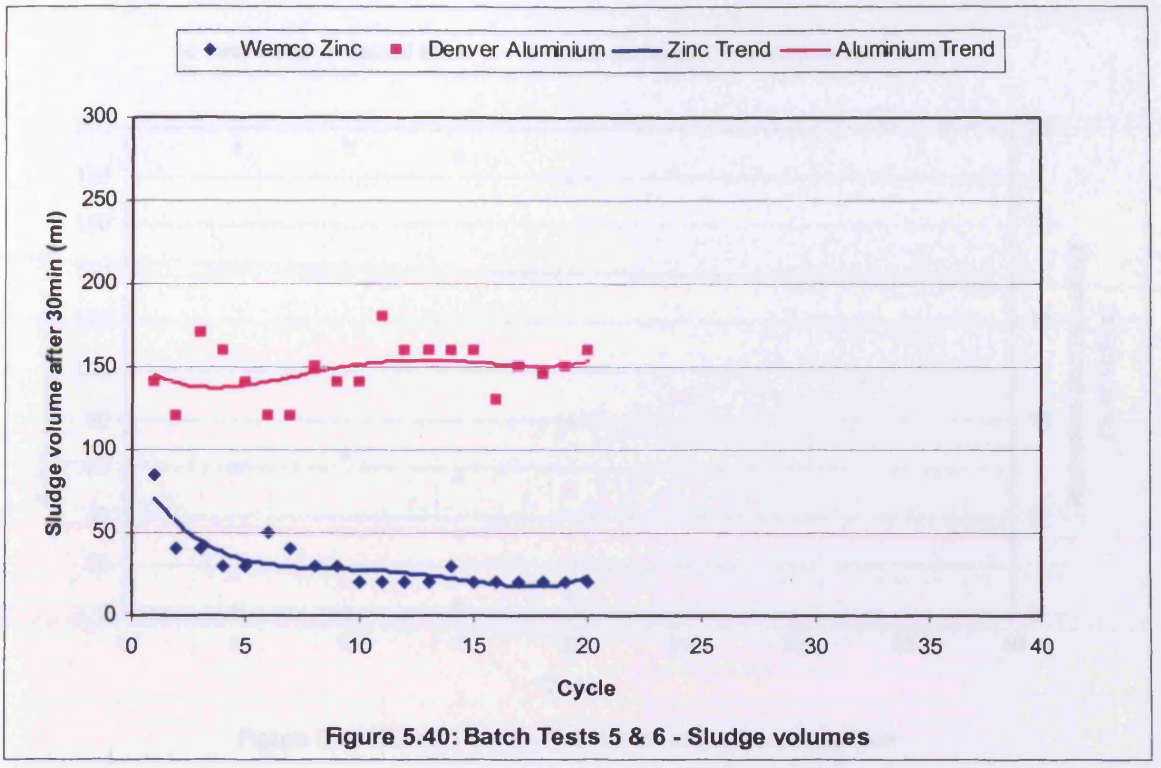


Figure 5.40: Batch Tests 5 & 6 - Sludge volumes

5.10.2 Batch Tests 5 and 6 – Sludge Composition

The variation in the initial and settled sludge solids concentration after 30 minutes in Batch Test 5 (synthetic zinc minewater) is presented in Table 5.19. This indicates that by the end of the test, the initial solids concentration was 3.84 g/l and the settled solids concentration was 196 g/l. The data also shows that the ratio of settled solids to initial sludge solids by the end of the test after 20 cycles was 51. The 'hydroxide' content of the sludge generated during the test was 20.9%, whilst the carbonate content was 13.3%.

The variation in the initial and settled solids concentration in Batch Test 6 (synthetic aluminium minewater) is shown in Figure 5.63 and presented in Table 5.20. This indicates that the settled solids concentration increased from 15.6 g/l at the start of the test, to 50.0 g/l at the end of the test. The data also shows that the ratio of settled solids to initial sludge solids changed from an initial 8.3 after cycle 5 to a ratio of 7.2 after cycle 20.

Figure 5.41 also indicates how the percentages of the carbonates and 'hydroxides' in the solids vary during the test. During the test, the 'hydroxide' content changed from an initial 24.0% to 22.3% at the end of the test, whilst the carbonate content increased from an initial 7.6% to 9.9% at the end of the test.

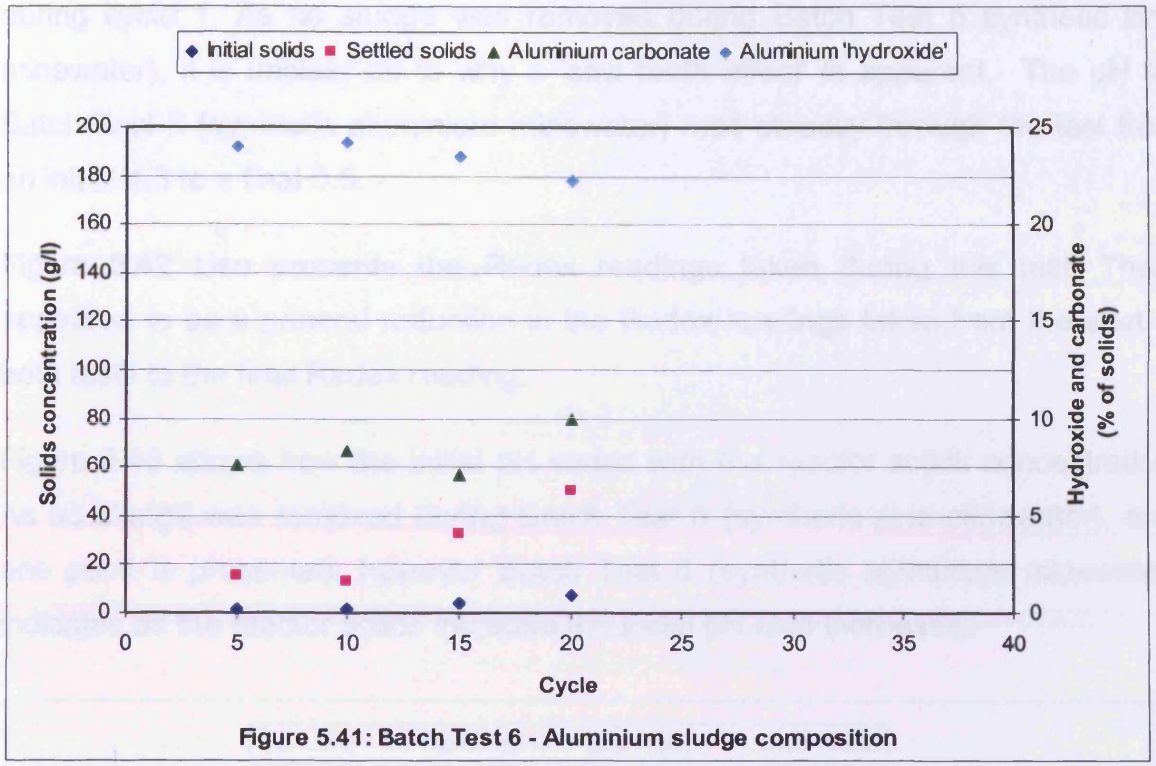


Figure 5.41: Batch Test 6 - Aluminium sludge composition

5.10.3 Batch Tests 5 and 6 – pH and Redox Readings

The Step 1 pH and Redox readings are presented in Figure 5.42.

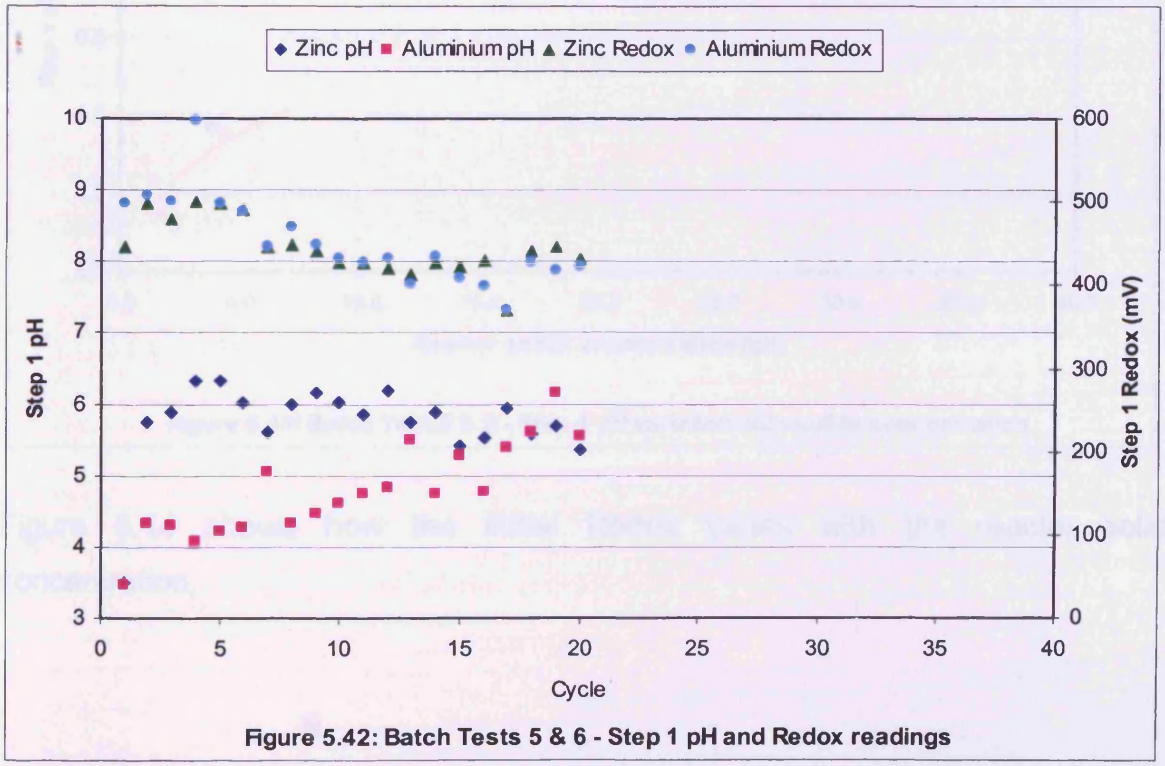


Figure 5.42: Batch Tests 5 & 6 - Step 1 pH and Redox readings

This shows that the Step 1 pHs for Batch Test 5 (synthetic zinc minewater) remained constant through the test at approximately 6.44, excluding the initial pH

during cycle 1. As no sludge was removed during Batch Test 5 synthetic zinc minewater), it is unclear as to why a 'saw tooth effect' is apparent. The pH for Batch Test 6 (synthetic aluminium minewater) rose steadily through the test from an initial 4.3 to a final 5.5.

Figure 5.42 also presents the Redox readings taken during this test. There appeared to be a general reduction in the Redox readings taken from the start of both tests to the final Redox reading.

Figure 5.43 shows how the initial pH varies with the reactor solids concentration. As no sludge was removed during Batch Test 5 (synthetic zinc minewater), only one point is presented, however Batch Test 6 (synthetic aluminium minewater) indicates as the reactor solids increase the initial pH also increases.

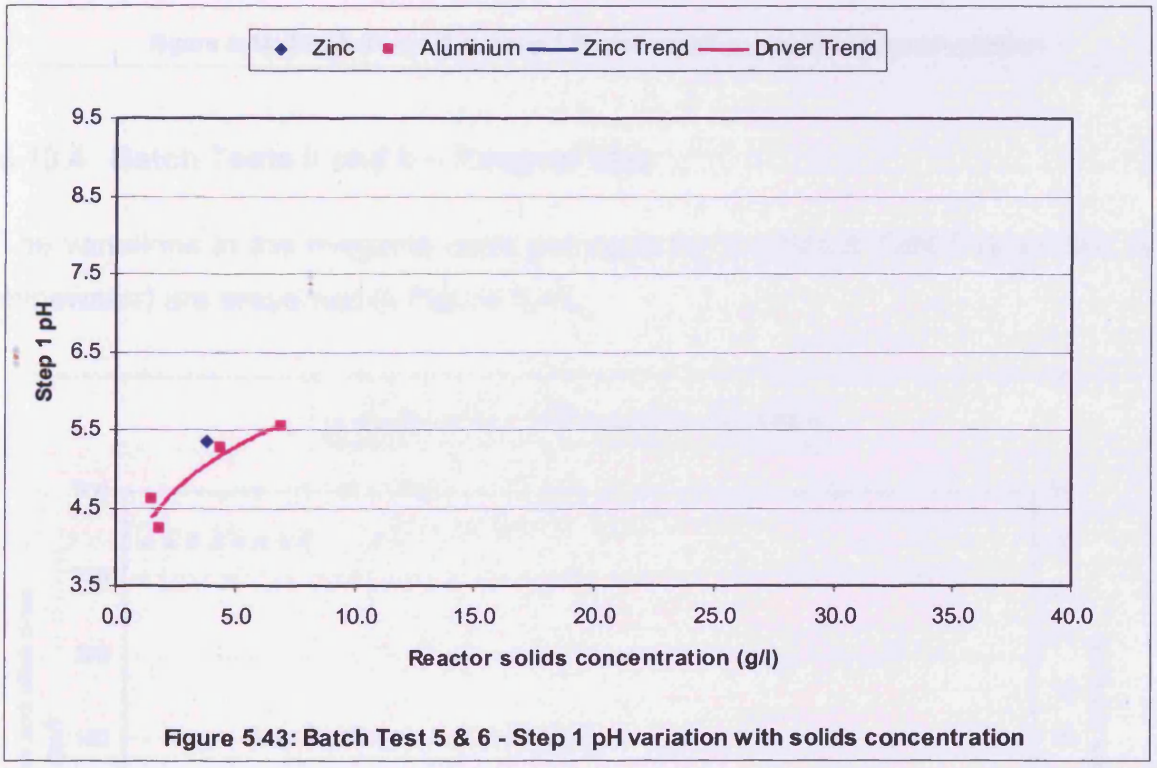


Figure 5.43: Batch Test 5 & 6 - Step 1 pH variation with solids concentration

Figure 5.44 shows how the initial Redox varies with the reactor solids concentration.

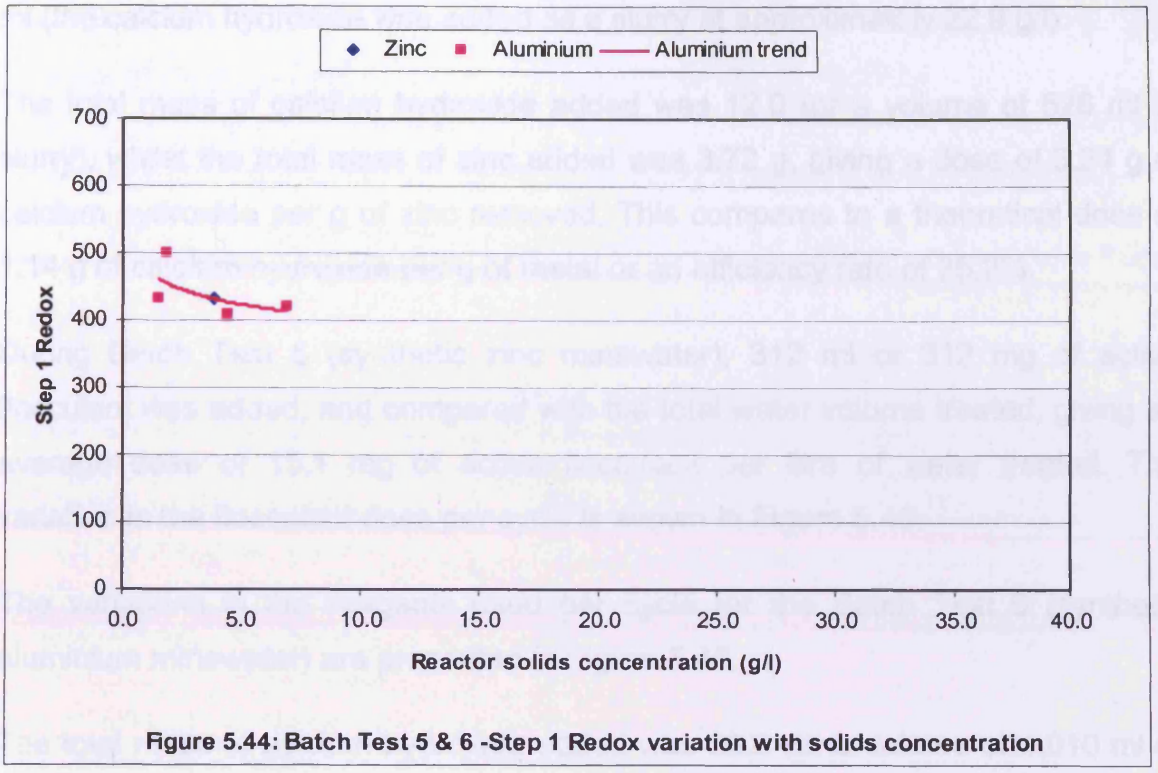


Figure 5.44: Batch Test 5 & 6 -Step 1 Redox variation with solids concentration

5.10.4 Batch Tests 5 and 6 – Reagent Use

The variations in the reagents used per cycle for the Batch Test 5 (synthetic zinc minewater) are presented in Figure 5.45.

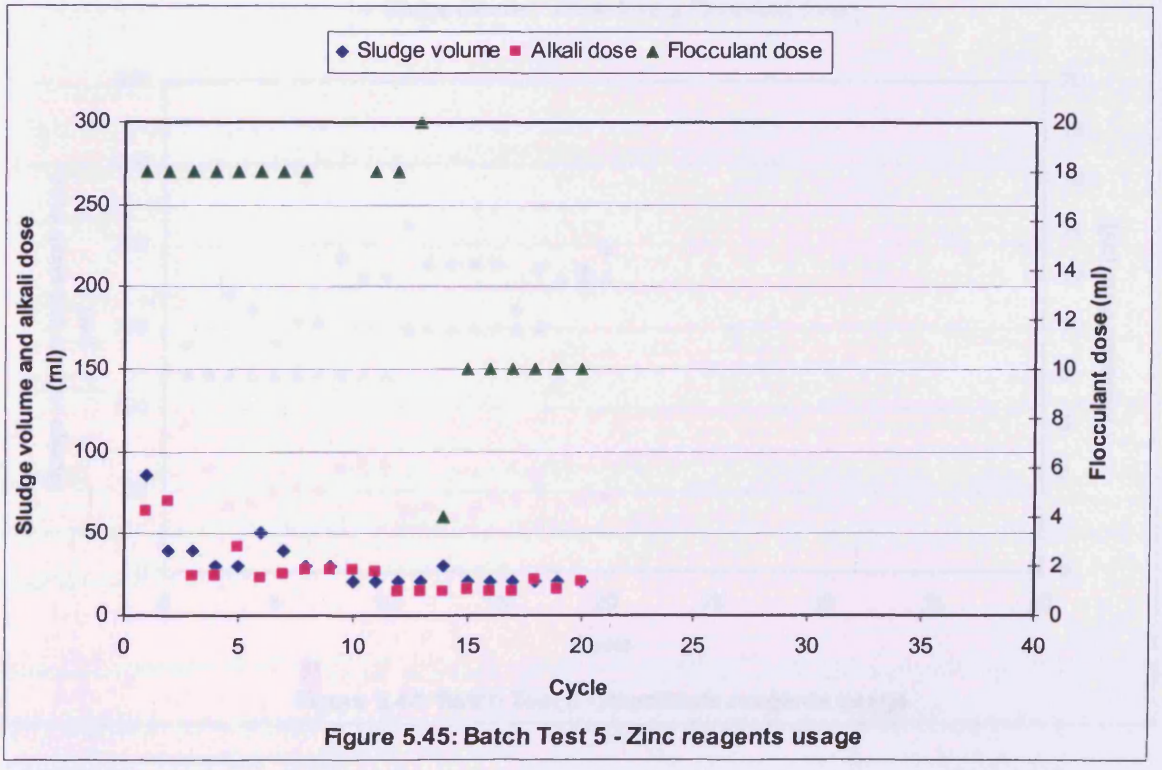


Figure 5.45: Batch Test 5 - Zinc reagents usage

The amount of alkali reagent, calcium hydroxide, added was recorded per cycle in

ml (the calcium hydroxide was added as a slurry at approximately 22.9 g/l).

The total mass of calcium hydroxide added was 12.0 (or a volume of 526 ml of slurry), whilst the total mass of zinc added was 3.72 g, giving a dose of 3.24 g of calcium hydroxide per g of zinc removed. This compares to a theoretical dose of 1.14 g of calcium hydroxide per g of metal or an efficiency rate of 35.2%.

During Batch Test 5 (synthetic zinc minewater), 312 ml or 312 mg of active flocculant was added, and compared with the total water volume treated, giving an average dose of 15.1 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.45.

The variations in the reagents used per cycle for the Batch Test 6 (synthetic aluminium minewater) are presented in Figure 5.46.

The total mass of calcium hydroxide added was 23.0 (or a volume of 1,010 ml of slurry), whilst the total mass of aluminium added was 3.1, giving a dose of 7.43 g of calcium hydroxide per g of aluminium removed. This compares to a theoretical dose of 4.12 g of calcium hydroxide per g of aluminium or an efficiency rate of 55.4%.

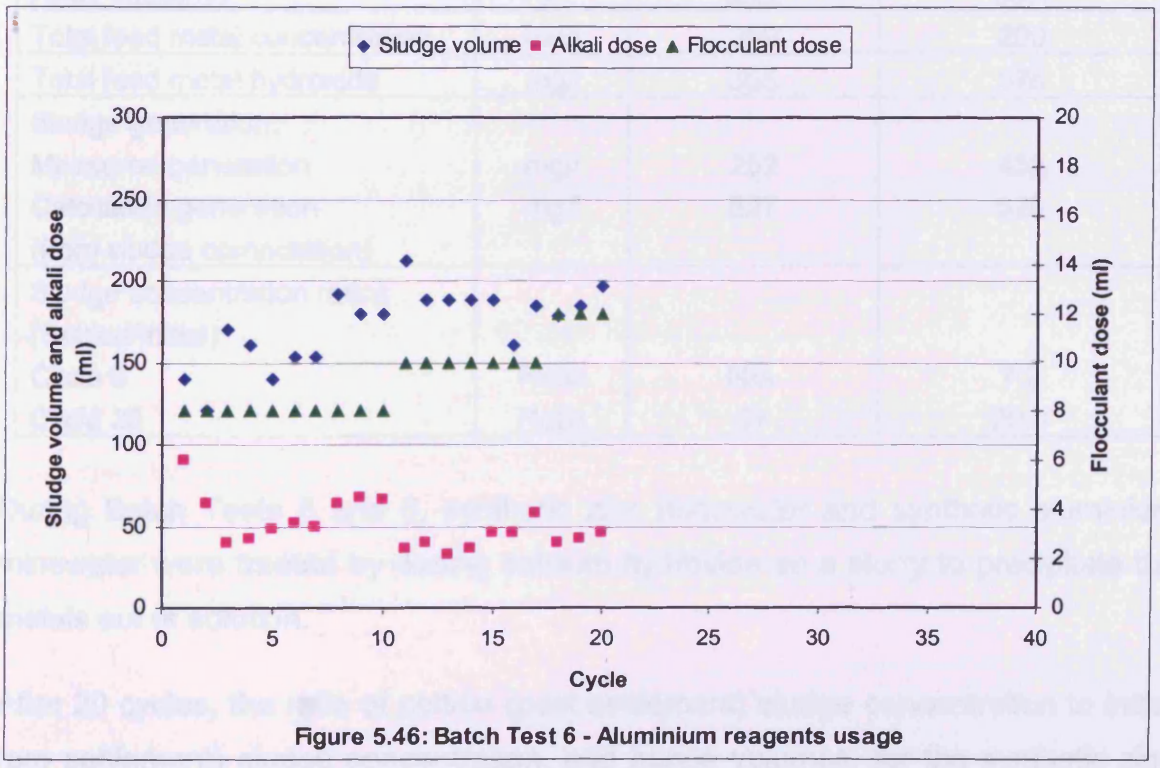


Figure 5.46: Batch Test 6 - Aluminium reagents usage

During Batch Test 6 (synthetic aluminium minewater), 186 ml or 186 mg of active flocculant was added, and compared with the total water volume treated, giving an

average dose of 8.10 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.46.

5.10.5 Batch Tests 5 and 6 – Summary of Key Performance Parameters

The key performance indicators of Batch Tests 5 and 6 are presented in Table 5.21.

Table 5.21: Batch Test 5 and 6 Key Performance Parameters

Parameter	Unit	Zinc Test	Aluminium Test
Maximum sludge Volume	ml	85	212
No of Cycles (max volume)	No	1	11
Minimum sludge Volume	ml	<20	160
No of Cycles (Min volume)	No	10	16
Final Sludge Concentration	g/l	196	50
% of solid as Carbonate	%	20.9	9.9
% of solid as Hydroxide	%	13.3	22.2
Flocculant dose	mg/l	15	8.1
Stage I pH	pH unit	5.58	5.45
Stage II pH	pH unit	6.20	6.25
Alkali used (calcium hydroxide)	ml	526	1010
Alkali usage (calcium hydroxide)	mg/l	602	1150
Alkali efficiency	%	35.2	55.4
Total feed metal concentration	mg/l	200	200
Total feed metal hydroxide	mg/l	305	578
Sludge generation: Measured generation Calculated generation (from sludge composition)	 mg/l mg/l	 252 527	 452 626
Sludge concentration ratios (Settled/Initial) Cycle 5 Cycle 20	 Ratio Ratio	 N/A 51	 7.2 20.0

During Batch Tests 5 and 6, synthetic zinc minewater and synthetic aluminium minewater were treated by dosing calcium hydroxide as a slurry to precipitate the metals out of solution.

After 20 cycles, the ratio of settled (post settlement) sludge concentration to initial (pre settlement) sludge concentration, and hence volumes, for the synthetic zinc minewater was 51. The ratio of settled (post settlement) sludge concentration to initial (pre settlement) sludge concentration for the synthetic aluminium minewater

had increased from an initial 7.2, after 5 cycles, to 20, after 20 cycles. It was therefore concluded that HDS sludge had been generated during both Batch Tests 5 and 6.

5.11 Batch Tests 7, 8 and 9 – Synthetic Iron in Seawater Minewater Treated with Calcium Hydroxide, Sodium Hydroxide and Sodium Carbonate

During Batch Tests 7, 8 and 9, 25 cycles were undertaken with the feed water presented in Table 5.22.

Table 5.22: Batch Tests 7, 8 and 9 Water Quality Summary

Sample	pH	Solids mg/l	Fe Mg/l	SO_4 mg/l	Ca mg/l
Feed water	7.6	1,750	228	5,600	1,580

In Batch Test 7, synthetic iron in seawater minewater was treated with sodium hydroxide, calcium hydroxide was used in Batch Test 8, whilst sodium carbonate was used in Batch Test 9. The Wemco flotation cell was used during the three batch tests.

The objective of Batch Tests 7, 8 and 9 was to see if a graph similar to that presented in Figure 5.1 could be obtained, therefore, no sludge samples were analysed during the three batch tests, hence the sludge masses and concentrations have not been presented.

5.11.1 Batch Tests 7, 8 and 9 – Sludge Volumes

Figure 5.47 presents the volume occupied by the sludge generated during the three batch tests.

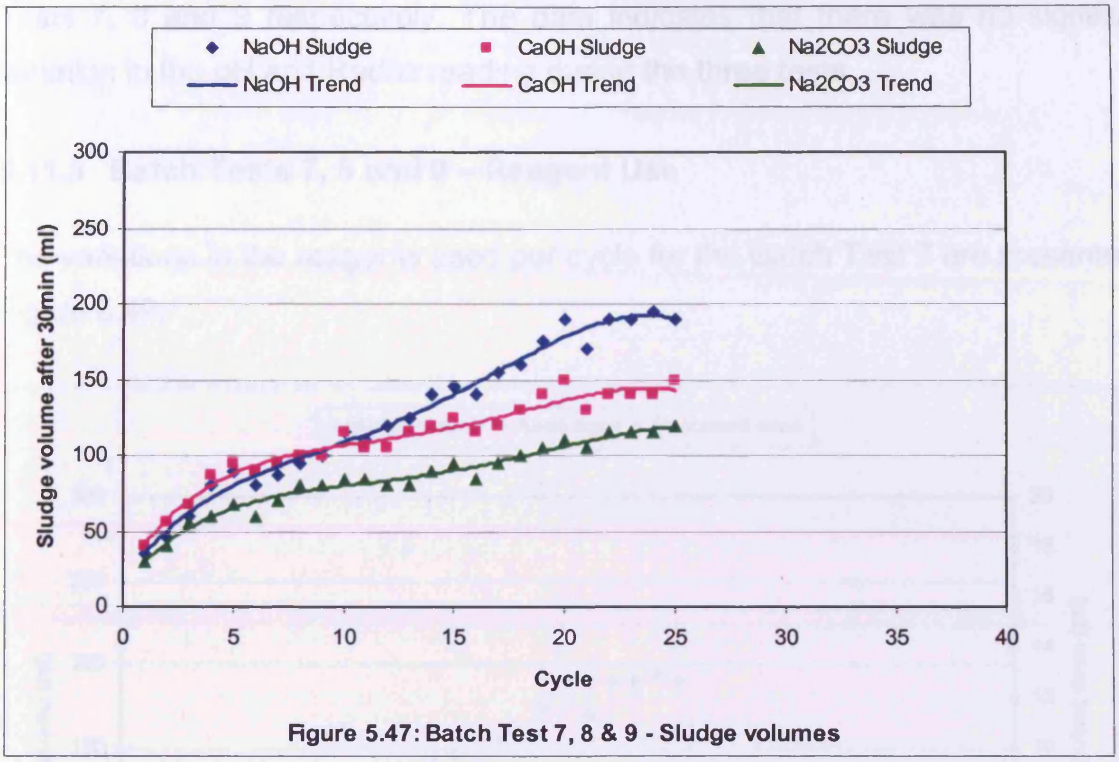


Figure 5.47: Batch Test 7, 8 & 9 - Sludge volumes

5.11.2 Batch Tests 7, 8 and 9 – pH and Redox Readings

The Step 1 pH and Redox readings are presented in Figure 5.48.

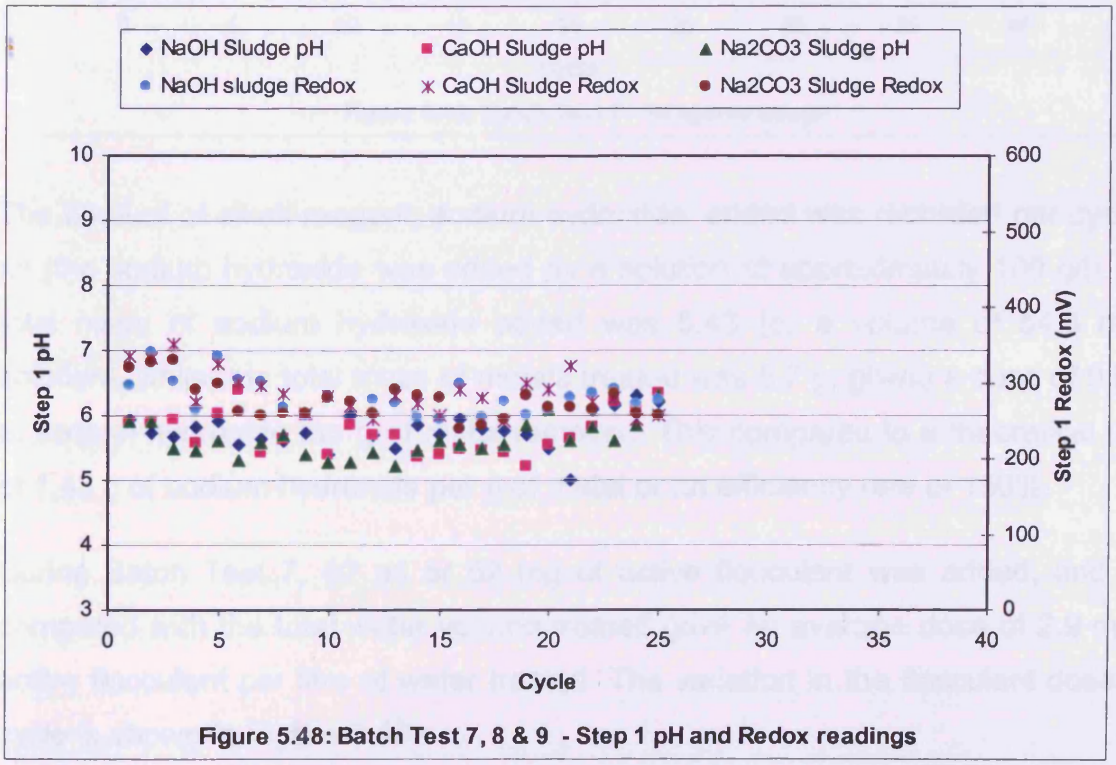


Figure 5.48: Batch Test 7, 8 & 9 - Step 1 pH and Redox readings

The average Step 1 pH values were 6.19, 6.23 and 6.18 for Batch Tests 7, 8 and 9 respectively. The average Step 1 Redox values were 282, 287 and 276 for Batch

Tests 7, 8 and 9 respectively. The data indicates that there was no significant variation in the pH and Redox reading during the three tests.

5.11.3 Batch Tests 7, 8 and 9 – Reagent Use

The variations in the reagents used per cycle for the Batch Test 7 are presented in Figure 5.49.

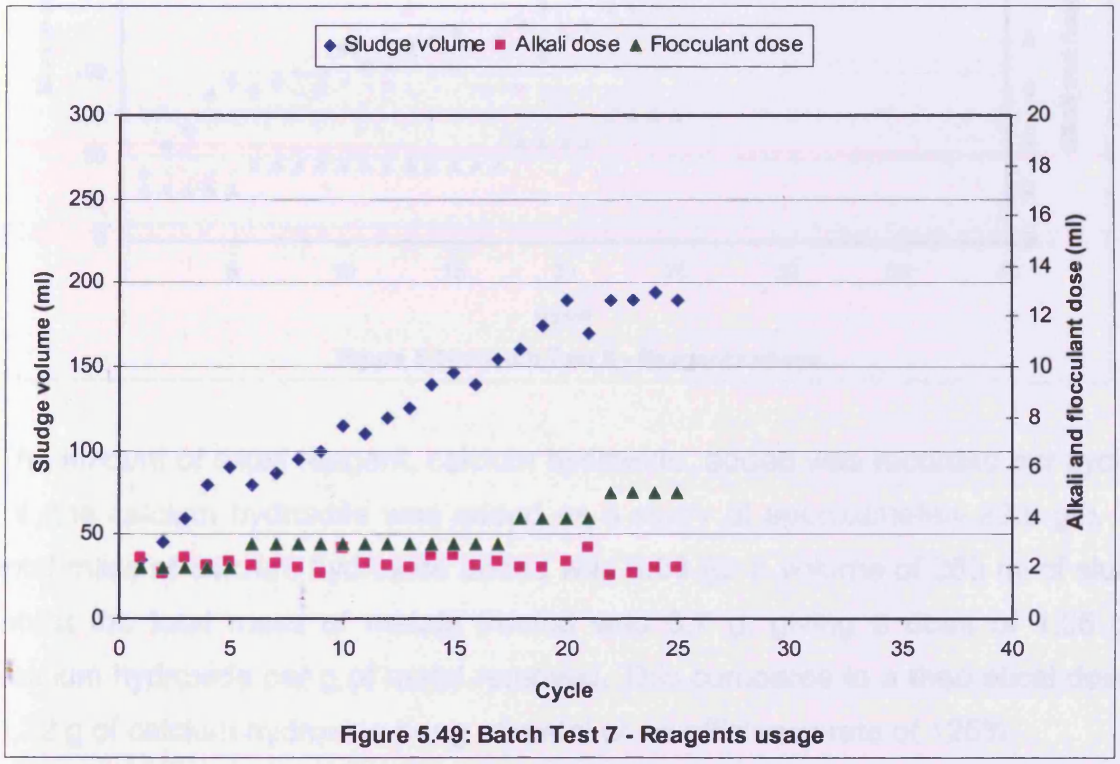


Figure 5.49: Batch Test 7 - Reagents usage

The amount of alkali reagent, sodium hydroxide, added was recorded per cycle in ml (the sodium hydroxide was added as a solution at approximately 100 g/l). The total mass of sodium hydroxide added was 5.43 (or a volume of 54.3 ml of solution), whilst the total mass of metals treated was 5.7 g, giving a dose of 0.95 g of sodium hydroxide per g of metal removed. This compares to a theoretical dose of 1.43 g of sodium hydroxide per g of metal or an efficiency rate of 150%.

During Batch Test 7, 82 ml or 82 mg of active flocculant was added, and that compared with the total water volume treated gave an average dose of 2.9 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.49.

The variations in the reagents used per cycle for the Batch Test 8 are presented in Figure 5.50.

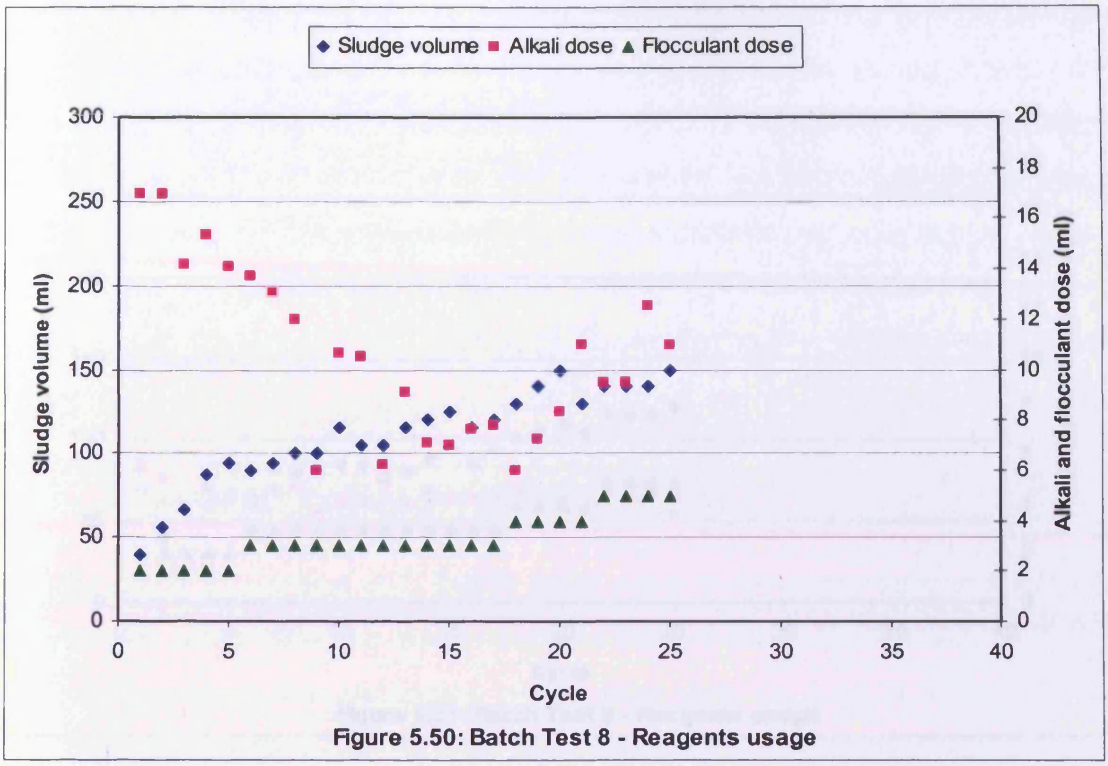


Figure 5.50: Batch Test 8 - Reagents usage

The amount of alkali reagent, calcium hydroxide, added was recorded per cycle in ml (the calcium hydroxide was added as a slurry at approximately 22.9 g/l). The total mass of calcium hydroxide added was 6.03 (or a volume of 263 ml of slurry), whilst the total mass of metals treated was 5.7 g, giving a dose of 1.06 g of calcium hydroxide per g of metal removed. This compares to a theoretical dose of 1.32 g of calcium hydroxide per g of metal or an efficiency rate of 125%.

During Batch Test 8, 82 ml or 82 mg of active flocculant was added, and that compared with the total water volume treated gave an average dose of 3.0 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.50.

The variations in the reagents used per cycle for the Batch Test 9 are presented in Figure 5.51.

The amount of alkali reagent, sodium carbonate, added was recorded per cycle in ml (the sodium carbonate was added as a solution at approximately 100 g/l). The total mass of sodium carbonate added was 10.9 (or a volume of 109 ml of solution), whilst the total mass of metals treated was 5.7 g, giving a dose of 1.91 g of sodium carbonate per g of metal removed. This compares to a theoretical dose of 1.89 g of calcium hydroxide per g of metal or an efficiency rate of 99.2%.

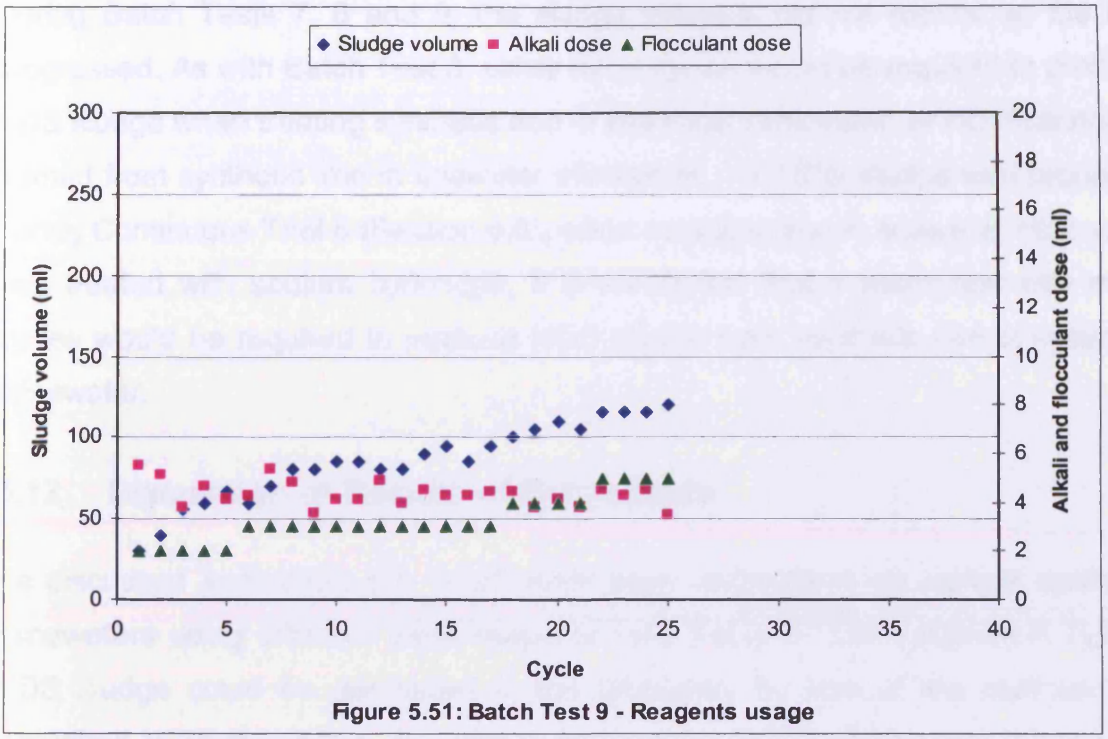


Figure 5.51: Batch Test 9 - Reagents usage

During Batch Test 9, 82 ml or 82 mg of active flocculant was added, and that compared with the total water volume treated gave an average dose of 3.0 mg of active flocculant per litre of water treated. The variation in the flocculant dose per cycle is shown in Figure 5.51.

5.11.4 Batch Tests 7, 8 and 9 – Summary of Key Performance Parameters

The key performance indicators of Batch Tests 7, 8 and 9 are presented in Table 5.23.

Table 5.23: Batch Tests 7, 8 and 9 Key Performance Parameters

Parameter	Unit	Sodium Hydroxide Sludge	Calcium Hydroxide Sludge	Sodium Carbonate Sludge
Maximum sludge Volume	ml	195	150	120
No of Cycles (max volume)	No	24	20	25
Minimum sludge Volume	ml	N/A	N/A	N/A
No of Cycles (Min volume)	No	N/A	N/A	N/A
Flocculant dose	mg/l	2.91	2.95	3.02
Stage I pH	pH unit	6.3	6.3	6.3
Stage II pH	pH unit	8.16	7.69	7.98
Alkali used	ml	54.3	263	109
Alkali usage	mg/l	217	241	435
Total feed metal concentration	mg/l	200	200	200
Total feed metal hydroxide	mg/l	382	382	382

During Batch Tests 7, 8 and 9, the sludge volumes did not reduce as the test progressed. As with Batch Test 3, either more cycles would be required to produce HDS sludge when treating synthetic iron in seawater minewater, or HDS cannot be formed from synthetic iron in seawater minewater. As HDS sludge was produced during Continuous Trial 5 (Section 6.8), when synthetic iron in seawater minewater was treated with sodium hydroxide, it is concluded that a batch test with more cycles would be required to produce HDS sludge from synthetic iron in seawater minewater.

5.12 Discussion of Results of Batch Tests

As discussed in Section 5.1, batch tests were undertaken on various synthetic minewaters using different alkali reagents (see Table 5.1) to establish if Type II HDS sludge could be generated in the laboratory by use of the methodology described in Section 5.2.2. In order to understand if HDS sludge was formed it is necessary to review the volume occupied by the precipitated sludge.

As HDS sludge is generated at the Wheal Jane HDS MWTP (Chapter 2 and 3), where calcium hydroxide is used as the alkali reagent, it was decided to undertake the first batch test using similar test conditions to those used at Wheal Jane and compare Batch Test 1 results with those generated on the full-scale Wheal Jane HDS MWTP. The results of subsequent batch tests would be compared to the results of Batch Test 1 as a measure of the process efficiency.

5.12.1 Sludge Volumes

Figure 5.5 (see Section 5.6.1) shows that after an initial increase in volume occupied by the precipitated sludge, a decrease in the sludge volume was recorded. This decrease in sludge volume occurred after approximately 15 cycles, when the settlement characteristics appeared to change and no further increase in sludge volume was recorded, even though the mass of sludge was increasing. This is similar to the results reported by Bosman (1980) and confirmed that Type II HDS sludge had been formed during Batch Test 1. Similar graphs for the sludge generated during Batch Test 2 (Figure 5.14) and Batch Test 4 (Figure 5.30) also confirmed that Type II HDS sludge was formed during these tests. Hence Type II HDS sludge was generated on synthetic Wheal Jane minewater when calcium hydroxide, sodium hydroxide and sodium carbonate were used as the alkali

reagent.

The results of Batch Test 5 (Figure 5.40), the zinc test, showed a very quick reduction in sludge volume which possibly indicated that the formation of HDS sludge was very sudden.

The results of Batch Tests 3 (Figure 5.21), 6 (Figure 5.40, aluminium), 7, 8 and 9 (Figure 5.47) appeared to show that no reduction in the sludge volume was recorded. This could indicate that either HDS could not be formed or (and considered more likely) that the maximum sludge volume was not reached and hence more test cycles would be required to generate HDS sludge.

Presented in Table 5.24 is a comparison of the maximum and minimum volumes of the settled sludge and the number of cycles undertaken during each of the batch tests. Table 5.24 also shows that the Wemco cell produced sludge with a lower minimum settled volume than the Denver cell. During Batch Test 4 (when sodium carbonate was the alkali reagent) the lowest minimum volume was recorded.

Table 5.24: Comparison of sludge volumes generated during Batch Tests

Batch test	Sludge volume limits	Wemco cell		Denver cell	
		Volume (ml)	Cycle	Volume (ml)	Cycle
Test 1 – Synthetic Wheal Jane dosed with $Ca(OH)_2$	Maximum vol. Minimum vol.	265 126	11 27	231 157	16 24
Test 2 - Synthetic Wheal Jane dosed with NaOH	Maximum vol. Minimum vol.	250 141	7 30	319 176	7 30
Test 3 - Synthetic Wheal Jane dosed with $Mg(OH)_2$	Maximum vol. Minimum vol.	162 -	36 -	277 -	36 -
Test 4 - Synthetic Wheal Jane dosed with Na_2CO_3	Maximum vol. Minimum vol.	240 95	2 18	240 109	4 17

5.12.2 Batch Test Settled Sludge Concentrations

In Section 5.12.1 it has been shown that Type II HDS sludge was generated during Batch Test 1, 2, 4 and most likely during Batch Test 5. To confirm this, a comparison of the sludge concentrations pre and post settlement was undertaken, with the ratio of settled solids concentration to initial solids concentration

presented in Table 5.25. The ratios were calculated at the start of the tests (after cycle 5) and at the end of the test (typically after cycle 35).

Table 5.25: Comparison of sludge concentrations generated during batch tests

Batch test	Cycle Number	Wemco cell		Denver cell	
		Settled solids concentration (g/l)	Ratio settled solids / initial solids	Settled solids concentration (g/l)	Ratio settled solids / initial solids
Test 1 – Synthetic Wheal Jane dosed with $Ca(OH)_2$	Cycle 5 Cycle 35	16.5 124	7.5 16.3	16.2 84	7.8 12.0
Test 2 - Synthetic Wheal Jane dosed with NaOH	Cycle 5 Cycle 35	12.0 64	5.5 11.0	9.2 85.5	5.0 11.1
Test 3 - Synthetic Wheal Jane dosed with $Mg(OH)_2$	Cycle 5 Cycle 35	240 311	14.4 9.4	230 285	15.4 7.6
Test 4 - Synthetic Wheal Jane dosed with Na_2CO_3	Cycle 5 Cycle 30	18.3 118	6.8 17.7	15.3 103	5.9 15.2
Test 5 - Synthetic zinc dosed with $Ca(OH)_2$	Cycle 5 Cycle 20	- 196	- 51.0	- -	- -
Test 6 - Synthetic aluminium dosed with $Ca(OH)_2$	Cycle 5 Cycle 20	- -	- -	15.7 50	8.3 20.0

The ratios of the sludge generated in the Wemco cell were higher in all cases, with the exception of cycle 5 of test 3. As reported previously, this indicates that a sludge of enhanced settlement characteristics was generated by the Wemco cell, which was likely to have been caused by either increased shearing or increased introduction of carbonates due to the higher air flow rates.

For batch tests 1, 2, 4, 5 and 6, the ratio of settled solids concentration to initial solids concentration increased the longer the tests proceeded, confirming that HDS sludge was being formed. However, during Batch Test 3, the ratio decreased during the test, suggesting that by the end of the test, HDS sludge had not been formed. The excess solids, and particularly excess magnesium ions, present in Batch Test 3 may have 'swamped' the system and may have interfered with the formation of the HDS sludge.

The Wheal Jane MWTP ratio of settled solids to initial solids concentrations were calculated to be 11.9 for Stream 1 and 13 for Stream 2 (see Section 4.5.13 and

Table 4.8). These compare favourably with the results generated during Batch Test 1, hence it can be concluded that the methodology developed and presented in Section 5.2.2 can be used to confirm if Type II HDS can be formed by batch tests in the laboratory.

5.12.3 Solids Generation

The solids generation rate for each test was calculated with the results presented in Table 5.26.

The results for Batch Test 3 show that when magnesium hydroxide was used, the solid generation rate was 2,160 mg/l. This was approximately 4.5 times higher than the solids generation rate of Batch Test 1. This indicated that either not all the magnesium hydroxide added reacted during the testing, or that magnesium hydroxide does not raise the pH of the minewater to over a value of 9 efficiently. To achieve a pH of 9, excess magnesium hydroxide was required (confirmed by the poor alkali reagent efficiency, see Section 5.10.4) which also resulted in a very high solids generation rate.

Table 5.26: Comparison of batch test solid generation rates

Batch test	Wemco cell		Denver cell	
	Measured generation (mg/l)	Calculated generation (mg/l)	Measured generation (mg/l)	Calculated generation (mg/l)
Test 1 – Synthetic Wheal Jane dosed with $Ca(OH)_2$	485	561	446	516
Test 2 - Synthetic Wheal Jane dosed with NaOH	452	474	432	461
Test 3 - Synthetic Wheal Jane dosed with $Mg(OH)_2$	2,160	1,610	2,160	1,690
Test 4 - Synthetic Wheal Jane dosed with Na_2CO_3	693	613	524	586
Test 5 - Synthetic zinc dosed with $Ca(OH)_2$	252	527	-	-
Test 6 - Synthetic aluminium dosed with $Ca(OH)_2$	-	-	452	626

The Wheal Jane MWTP solids generation rate was measured at 760 mg/l and 720 mg/l for Stream 1 and Stream 2 respectively, which is between 28% and 47% higher than calculated solids generation rate for Batch Test 1. The lack of 'other'

impurities and chemical elements, e.g. carbon dioxide, would explain the differences in the solids generation rates.

5.12.4 Batch Test Sludge Chemical Composition

A key purpose of minewater treatment is to ensure the metal content of the sludge removed from the treatment process is as high as possible in order to reduce the volume of sludge to be disposed of. This can be achieved by increasing the total solids concentration of the sludge or by ensuring that the concentration of metals in the solids is as high as possible.

The samples of the sludge generated during the batch tests were analysed for sludge composition, with the results of the final analysis presented in Table 5.27.

The results for Batch Test 3 show the highest final settled solids concentrations, however, the sludge generated during Batch Test 3 contained high concentrations of hydroxide (measured as chemical water) and magnesium, indicating the presence of excess alkali reagent. This was also indicated by the low alkali reagent efficiency observed during Batch Test 3 (see Section 5.10.4). The high solids generated during Batch Test 3 resulted in the metal content of the sludge being lower than that measured during other batch tests. For example, iron was only 12.4% w/w (Wemco cell) and 11.8% w/w (Denver cell) of the solids generated during Batch Test 3, compared to 42.4% w/w (Wemco cell) and 42.4% w/w (Denver cell) of the solids in Batch Test 2 when the percentage of metals in the sludge where highest.

Table 5.27: Batch test final sludge composition

Batch test	Settled solids (g/l)	Fe (g/l)	Zn (g/l)	Mn (g/l)	Al (g/l)	Mg (g/l)	Ca (g/l)	Na (g/l)	SO_4 (g/l)	Hydroxide (g/l)	Carbonate (g/l)
Test 1 - Wemco	124	43.6	8.8	1.2	3.9	-	6.4	-	-	12.6	11.6
Test 1 - Denver	84.4	32.8	6.7	0.9	3.0	-	2.3	-	-	8.3	5.5
Test 2 - Wemco	64.0	27.1	5.7	1.0	2.3	-	-	<0.0	-	6.1	2.2
Test 2 - Denver	85.5	36.2	7.6	1.3	3.3	-	-	<0.0	-	8.6	2.0
Test 3 - Wemco	306	37.8	7.6	1.0	3.5	62.1	-	-	-	85.6	15.3
Test 3 - Denver	278	32.9	6.7	0.9	3.1	60.3	-	-	-	71.6	11.2
Test 4 - Wemco	118	42.3	7.4	-	4.1	-	<0.0	-	-	22.4	1.9
Test 4 - Denver	103	38.8	8.9	-	4.0	-	<0.0	-	-	15.1	3.0
Test 5 - Zn	196	1.1	69.2	-	0.2	-	8.9	-	1.4	40.8	25.9
Test 6 – Al	50.0	0.5	0.3	-	12.4	-	3.6	-	3.2	11.1	5.0

Table 5.27 also shows that the iron content of the sludge generated in Batch Test

5 was approximately 0.6% of the solids compared to 35% of the solids being zinc. This would indicate that iron does not have to be present to form HDS sludge.

During Batch Tests 2 and 5, the measured carbonate concentrations were lowest at between 1.6% and 3.4% of the total solids generated, indicating that the presence of high carbonate concentrations is not required to produce HDS sludge.

5.12.5 Scanning Electron Microscopy (SEM) Analysis

Sludge samples taken after cycle 5, 15 and 35 during Batch Tests 1, 2 and 3 were analysed by SEM (see Section 3.5.3). Two images of each of the sludges generated by the Wemco cell are presented (x 1,000 and x 5,000 magnification), with a scale line overlaid on each image for reference purposes.

Batch Test 1 – Synthetic Wheal Jane minewater treated with calcium hydroxide

The results of Batch Test 1 (Wemco) SEM analysis are presented in Figure 5.52.

The SEM images were manually inspected to review the difference in morphology between sludge of different cycles and to compare the sludge generated by different alkali reagents.

Figures 5.52a and 5.52b present the floc structure after 5 cycles and show a floc that is very 'open' in appearance. The floc aggregations appear to be made up of 'plates'. As the number of cycles increases, the aggregations appear to become more compact and dense in nature. Figures 5.52e and 5.52f, showing sludge from cycle 35, show more compact, denser aggregations, with large aggregations formed by the clumping together of the smaller aggregations, see Table 5.28. No crystalline structure is apparent in any of the images presented in Figure 5.52.

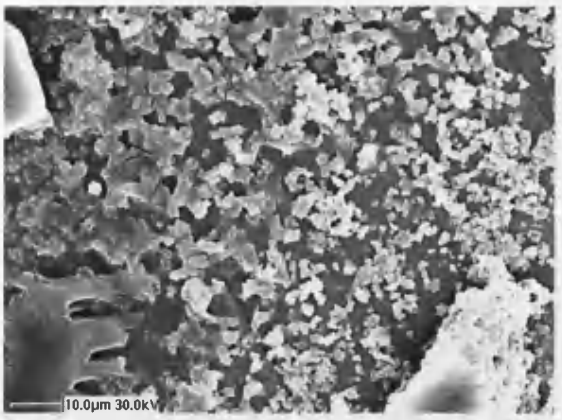


Figure 5.52a: Batch Test 1
5 cycle sludge – Magnification 1,000

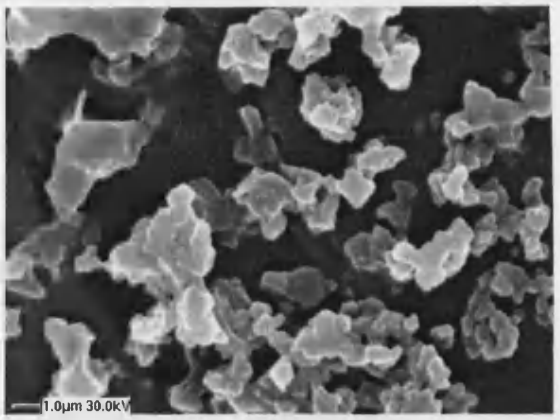


Figure 5.52b: Batch Test 1 -
5 cycle sludge – Magnification 5,000

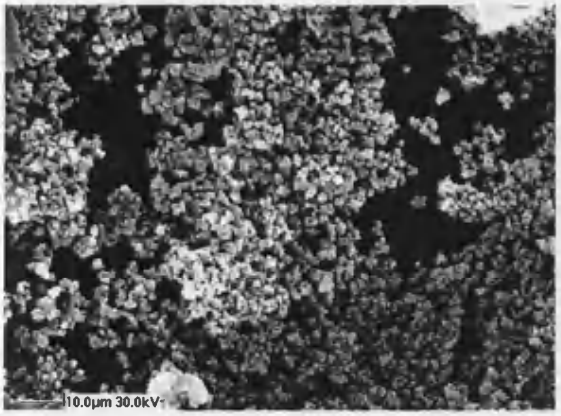


Figure 5.52c: Batch Test 1 -
15 cycle sludge – Magnification 1,000

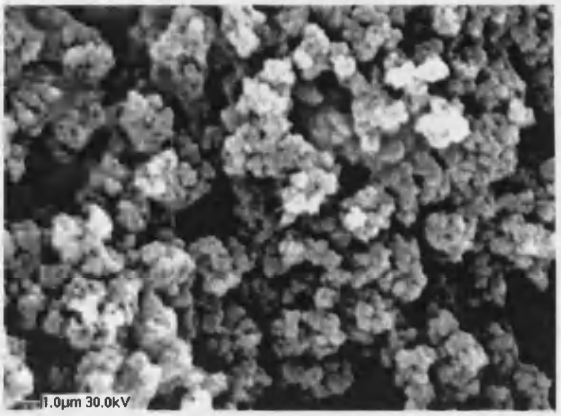


Figure 5.52d: Batch Test 1 -
15 cycle sludge – Magnification 5,000

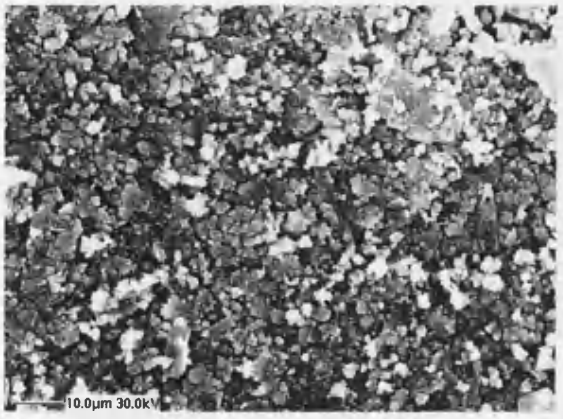


Figure 5.52e: Batch Test 1 -
35 cycle sludge – Magnification 1,000

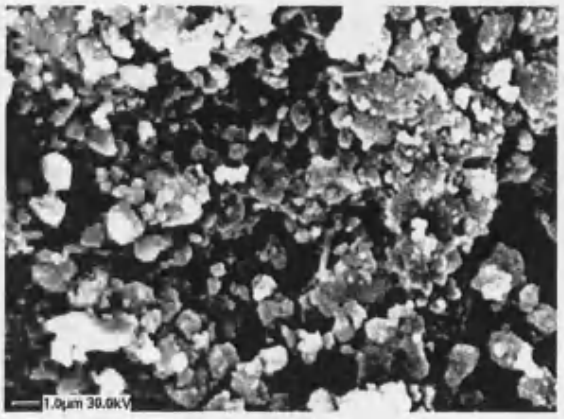


Figure 5.52f: Batch Test 1 -
35 cycle sludge – Magnification 5,000

Figure 5.52: Batch Test 1 – Wemco SEM

The results of the SEM analysis of Batch Test 1 (Denver) are presented in Figure 5.53 and do not differ significantly from those generated by the Wemco cell. Due to the image capture technique used, Figure 5.53b is slightly blurred.

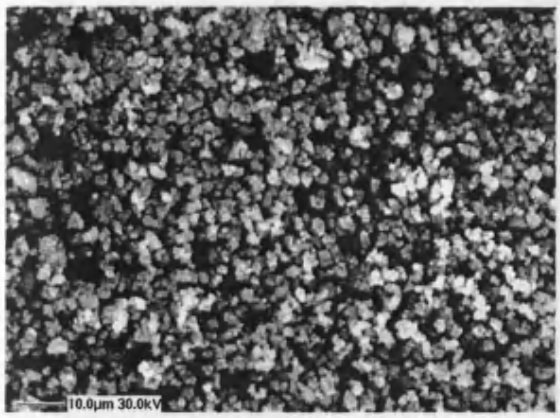


Figure 5.53a Batch Test 1 -
35 cycle sludge – Magnification 1,000

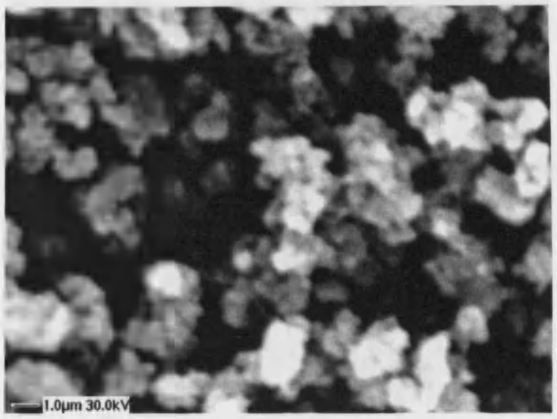


Figure 5.53b Batch Test 1 -
35 cycle sludge – Magnification 5,000

Figure 5.53: Batch Test 1 – Denver SEM

Batch Test 2 – Synthetic Wheal Jane minewater treated with sodium hydroxide

The results of the SEM analysis of Batch Test 2 (Wemco) are presented in Figure 5.54. As with the images for Batch Test 1, two images of each of the sludges generated by the Wemco cell are presented (x 1,000 and x 5,000 magnification).

Figures 5.54a and 5.54b present the floc structure after 5 cycles, with the floc structure being made up of very large plate like aggregates. As the number of cycles increases the aggregations appear to become smaller and more similar to those generated during Batch Test 1, see Table 5.28. Figures 5.54e and 5.54f, sludge from cycle 35, show a floc made up of much smaller compact aggregations.

No crystalline structure is apparent in any of the images presented in Figure 5.54.

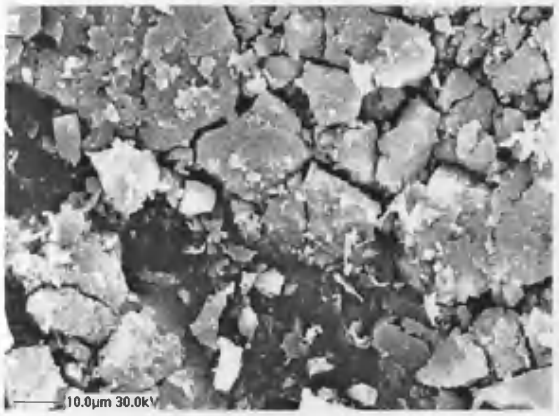


Figure 5.54a: Batch Test 2 -
5 cycle sludge – Magnification 1,000

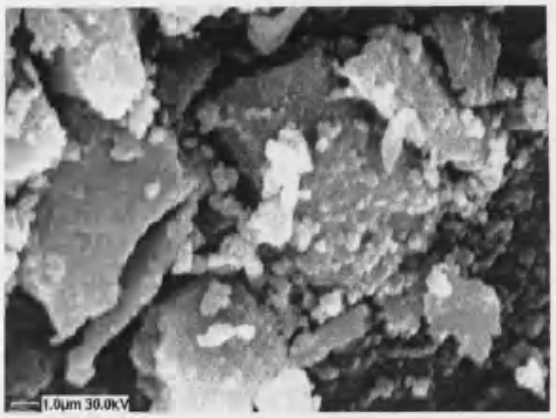


Figure 5.54b: Batch Test 2 -
5 cycle sludge – Magnification 5,000

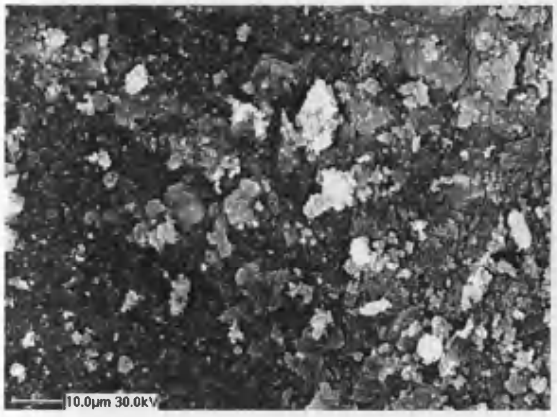


Figure 5.54c: Batch Test 2 -
15 cycle sludge – Magnification 1,000

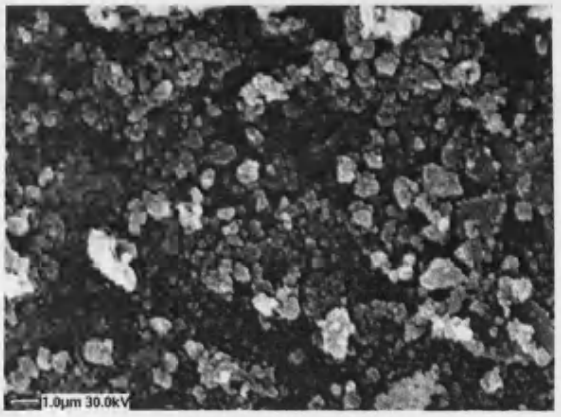


Figure 5.54d: Batch Test 2 -
15 cycle sludge – Magnification 5,000

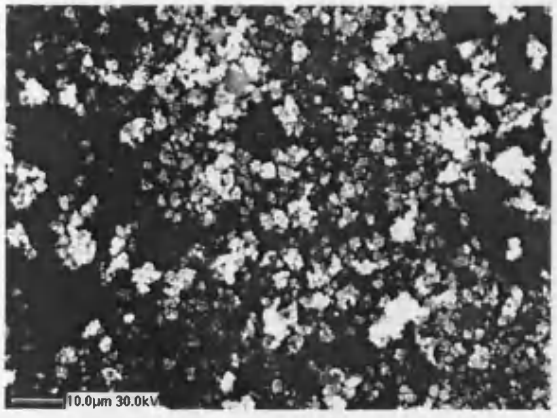


Figure 5.54e: Batch Test 2 -
35 cycle sludge – Magnification 1,000

Figure 5.54f: Batch Test 2 -
35 cycle sludge – Magnification 5,000

Figure 5.54: Batch Test 2 – Wemco SEM

Batch Test 3 – Synthetic Wheal Jane minewater treated with magnesium hydroxide

The results of the SEM analysis of Batch Test 3 are presented in Figure 5.55. As with the images for Batch Test 1 and 2, two images of each of the sludges generated by the Wemco cell are presented (x 1,000 and x 5,000 magnification).

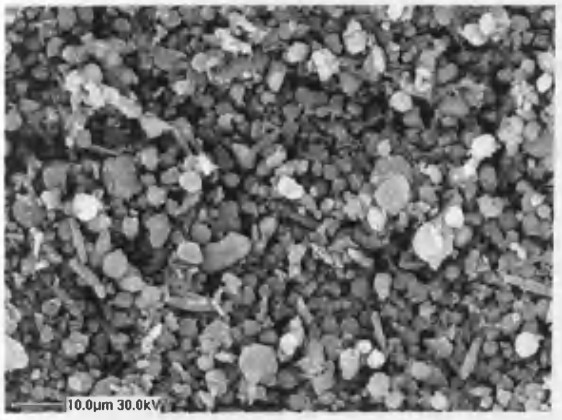


Figure 5.55a: Batch Test 3 -
5 cycle sludge – Magnification 1,000

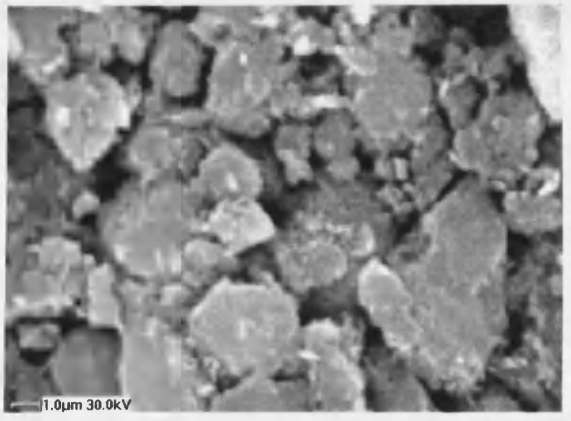


Figure 5.55b: Batch Test 3 -
5 cycle sludge – Magnification 5,000

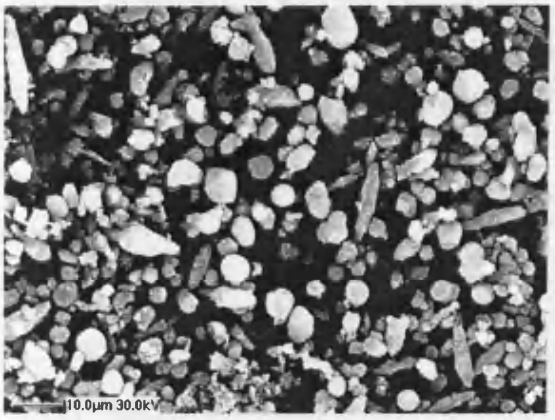


Figure 5.55c: Batch Test 3 -
15 cycle sludge – Magnification 1,000

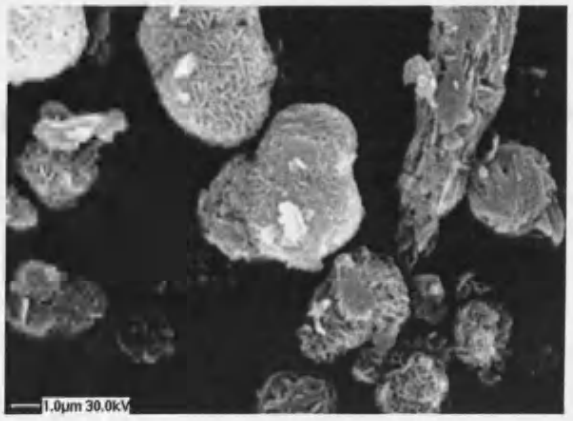


Figure 5.55d: Batch Test 3 -
15 cycle sludge – Magnification 5,000

Figure 5.55e: Batch Test 3 -
35 cycle sludge – Magnification 1,000

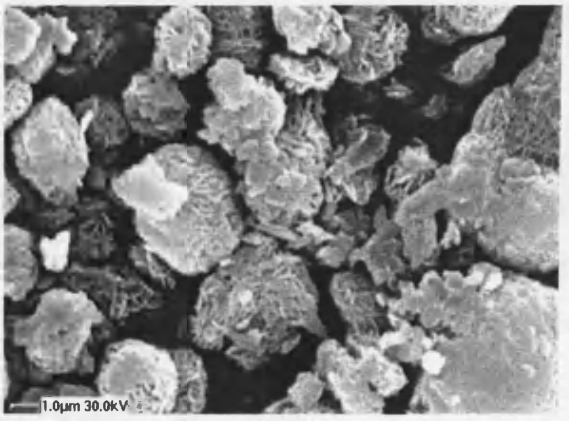


Figure 5.55f: Batch Test 3 -
35 cycle sludge – Magnification 5,000

Figure 5.55: Batch Test 3 – Wemco SEM

Figures 5.55a and 5.55b present the floc structure after 5 cycles, with the floc structure being made up of very large aggregates, spherical in appearance, see Table 5.28. On detailed inspection, the spherical aggregates are made up of smaller 'plates'. As the number of cycles increases, the definition of the aggregations increases with a 'dessert rose' appearance starting to form, Figure

5.55c. Figures 5.55e and 5.55f, sludge from cycle 35, shows that the aggregates have grown in size and can clearly be seen to be made up of numerous 'plates'.

Again no crystalline structure is apparent in any of the images presented in Figure 5.56.

Summary of SEM analysis

A summary of the SEM analysis undertaken is presented in Table 5.28.

Table 5.28: Comparison of SEM analysis of all sludges analysed

Trial Number	'Young' sludge		'Old' sludge		Comments on aggregates
	Average size μm	Maximum size μm	Average size μm	Maximum size μm	
Batch Test 1	2	5	2	4	Fine, small and dispersed
Batch test 2	10	20	2	4	Young -Platy, massive Old – Small, compact
Batch test 3	5	10	4	8	Spherical, with the appearance of 'dessert rose'

As Batch Test 1 progressed, the aggregates produced became more compact in nature compared to the more 'platy' 'young' sludge. The size of the aggregates, however, did not vary greatly as the test proceeded.

In contrast to Batch Test 1, the aggregates generated during Batch Test 2 reduced in size as the test proceeded, with the 'old' sludge aggregates being approximately 20% of the size of the 'young' sludge aggregates. As with Batch Test 1, the sludge aggregates transformed from being 'platy' in appearance to more compact sludge aggregates as the test proceeded.

The sludge aggregates produced during Batch Test 3 grew as the test continued, and became the largest 'old' sludge analysed. The aggregates were made up of numerous plates which gave a 'dessert rose' appearance.

5.12.6 Batch Test Conclusions

The batch tests were undertaken to confirm that HDS could be formed in the laboratory on synthetic minewater by using the Type II HDS process and by using different alkali reagents.

Test Objective 1: Generate Type II HDS sludge by undertaking batch tests on synthetic minewater.

The Batch Test 1 was undertaken to see if Type II HDS sludge could be generated in the laboratory using synthetic Wheal Jane minewater with calcium hydroxide used as the alkali reagent. By undertaking more than 10 cycles, an initial change in the sludge characteristics (i.e. a reduced sludge volume) was observed and by undertaking in excess of 25 cycles, HDS sludge was formed (as defined by Bosman, 1980). It is therefore concluded that Type II HDS sludge can be generated in the laboratory using a cyclic batch test system. As ratios of settled solids concentration to initial solids concentration measured during Batch Test 1 (where ratios of 12.0 to 16.3 were measured) and those generated on the Wheal Jane MWTP (where ratios of 11.9 to 13.0 were measured) were comparable it is concluded the batch test methodology devised effectively mimicked the Wheal Jane MWTP HDS process in the laboratory.

Test Objective 2: Show that Type II HDS sludge could be formed using various alkali reagents.

By undertaking batch tests on the synthetic Wheal Jane minewater, using different alkali reagents (sodium hydroxide, sodium carbonate and magnesium hydroxide), the formation of HDS sludge by non-calcium based alkali reagents was investigated. The results for the sodium hydroxide and sodium carbonate batch tests yielded similar results to those when calcium hydroxide was used. It was therefore concluded that Type II HDS sludge can be formed using sodium hydroxide and sodium carbonate. However, when magnesium hydroxide was used HDS was not formed in the number of cycles undertaken.

Test Objective 3: Demonstrate that Type II HDS could be formed by non or low iron feed water.

To investigate if Type II HDS sludge could be generated from non-or low iron minewater, zinc and aluminium based synthetic minewaters were tested during two batch tests. The ratios of settled sludge to initial sludge concentrations for the both synthetic zinc and aluminium minewaters were greater than those for the synthetic Wheal Jane minewater. It was therefore concluded that HDS sludge could be generated from synthetic zinc and aluminium minewaters and that iron need not be present in the minewater to form HDS sludge.

Test Objective 4: Investigate the effect of seawater on the formation of Type II HDS.

The batch tests were undertaken on iron based synthetic minewater made from seawater to see if HDS sludge could be generated in the laboratory using different alkalis. In comparison to the tests undertaken on the synthetic Wheal Jane minewater, when HDS sludge was formed, it was concluded that in the number of cycles undertaken during Batch Tests 7, 8 and 9 HDS was not formed.

In addition, the following can be summarised from the batch tests:

1. Very low concentrations of carbonate were detected in the sludges generated during Batch Tests 2 and 4, which indicates that significant concentrations of carbonate are not required to form HDS sludge.

2. HDS sludge was not formed after 35 cycles of the batch test when magnesium hydroxide was used as the alkali reagent. This possibly indicates that when high concentrations of other elements are present, HDS sludge takes longer to form.

3. During the batch tests, the sludge generated appeared to have no crystalline structure and hence HDS sludge was formed by aggregation of the floc particles and not by crystallisation for the conditions investigated.

6 LABORATORY STUDIES – CONTINUOUS TRIALS

6.1 Introduction and Objectives

The results of the batch tests, Chapter 5, indicated that HDS could be formed using sodium hydroxide as the alkali reagent and by using non-Fe (II) metal solutions. As the batch tests were stopped after approximately 35 cycles, a series of laboratory continuously fed pilot plant trials were undertaken. The trials were to be used to confirm that HDS could be produced using; sodium hydroxide as the alkali reagent, feed water without iron present and to generate data to further the understanding the characteristics of HDS sludge. Four different metal feed solutions were used: iron, zinc, aluminium and manganese. Additionally, iron was dissolved in seawater as well as tap water. A final trial, using a mixed metals solution as the feed source, was also undertaken. Table 6.1 lists the trials, the metal, the trial period, the chosen operating pH and the alkali reagent used during the trial.

Table 6.1: List of pilot plant trials

Trial No	Trial Description	Start	Finish	Operating pH	Alkali Used
1	Iron in tap water	19 Sept 03	06 Oct 03	9.25	NaOH
2	Zinc in tap water	10 Nov 03	28 Nov 03	7.5 then 8.5	NaOH
3	Aluminium in tap water	01 Dec 03	19 Dec 03	6.0 then 6.9	NaOH
4	Manganese in tap water	11 March 04	30 March 04	9.25	NaOH
5	Iron in seawater	07 Oct 03	04 Nov 03	9.25 then 8.5	NaOH
6	Mixed metals in tap water	11 Dec 04	05 March 04	6.5 then 9.25	$Ca(OH)_2$

The objectives of the continuous trials were to:

1 Operate a laboratory pilot plant to generate Type II HDS sludge from various synthetic minewater using sodium hydroxide as the alkali reagent and note the difference in the sludge settlement characteristics.
2 Show that Type II HDS sludge can be generated from synthetic iron in seawater minewater using sodium hydroxide as the alkali reagent.
3 Examine the differences in behaviour between synthetic minewater containing bivalent and trivalent metals in solution.
4 Generate Type II HDS sludge from various synthetic minewaters and examine the difference in the sludge properties.

The pilot plant was set up as a Type II HDS process (Coulton *et al.* (2003 a), Coulton *et al.* (2003 b)), i.e. the recirculated sludge and the minewater were mixed prior to the addition of the alkali reagent and air. The pilot plant was sized to ensure that a comparison could be made between the pilot plant operating parameters and the operating parameters of the full-scale Type II Wheal Jane HDS MWTP, described in Section 4.1, Chapter 4. The operating pH of 9.25 was chosen for trials 1, 4 and 6 to match the operating pH of the Wheal Jane MWTP, where there is a requirement to remove manganese from the minewater. Metal feed concentrations of circa 200 mg/l were used to ensure metal feed concentrations comparable to those treated at the Wheal Jane MWTP.

6.2 Plant Description

The plant layout is shown schematically in Figure 6.1. A photograph of the pilot plant can also be seen in Figure 6.2. The process stream consists of a feed water storage tank reservoir and feed pump, concentrate iron solution storage and pump (for iron trials only), feed mixing chamber (required for iron trials), Stage I Reactor tank, Stage II Reactor, flocculation tank and a clarifier. Ancillary equipment comprised of alkali reagent (sodium hydroxide and calcium hydroxide) and flocculant, storage and dosing systems and air supply (for metal oxidation). A flow rate of 10 litres /hour was chosen, giving a nominal flow (excluding recycle flow) 30 minute retention time (as at Wheal Jane MWTP) using 5 litre reaction vessels.

A brief description of each stage of the pilot plant now follows. Where changes were made to the pilot plant during each trial, these are explained in the individual trial sections.

6.2.1 Influent Water Collection, Storage and Pumping

A $1m^3$ Intermediate Bulk Container (IBC) was used as a feed water storage tank reservoir. The chemical composition of the IBC full of tap water or seawater was adjusted to simulate the various influent water characteristics.

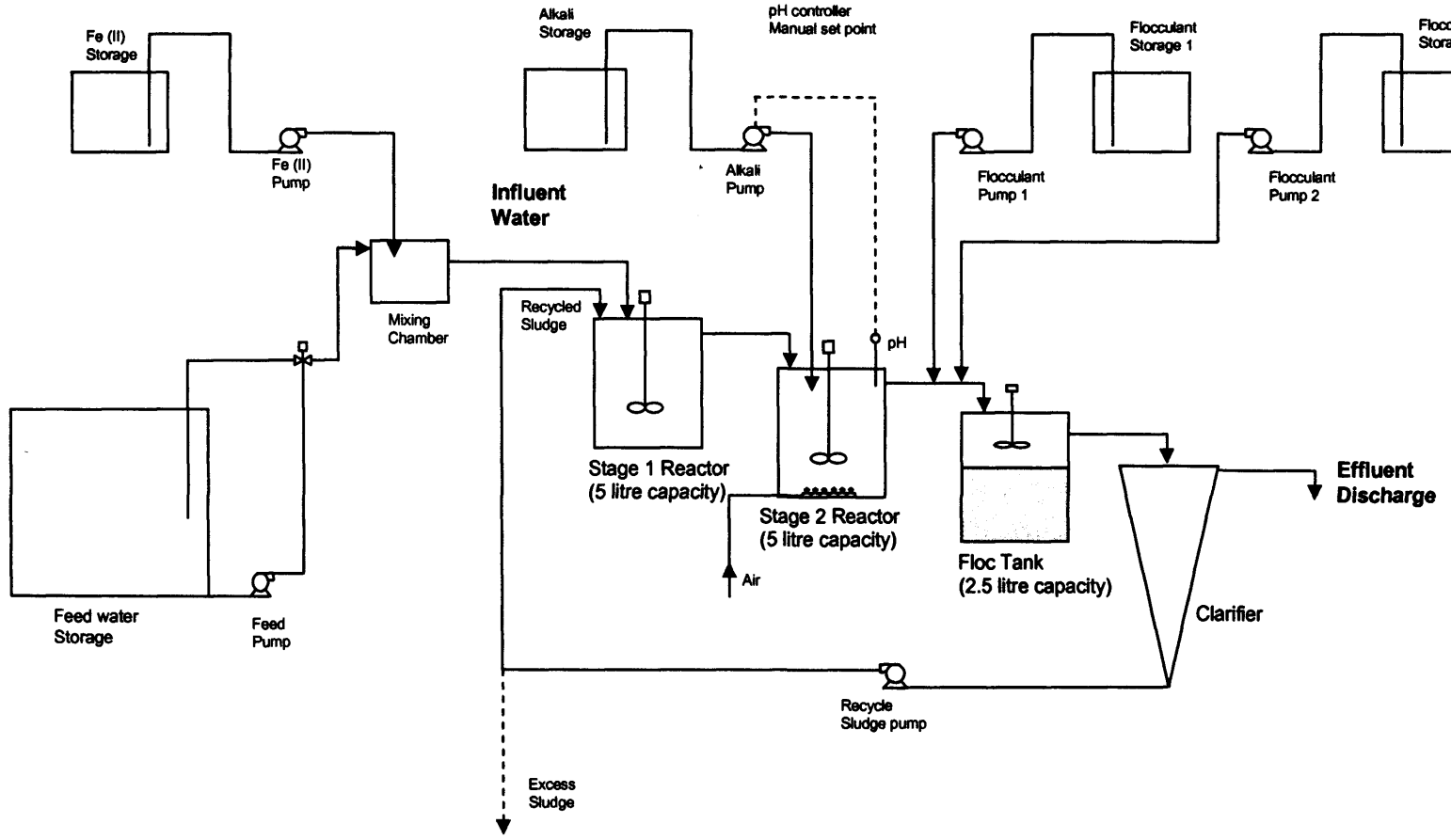


Figure 6.1: Schematic layout of the pilot plant

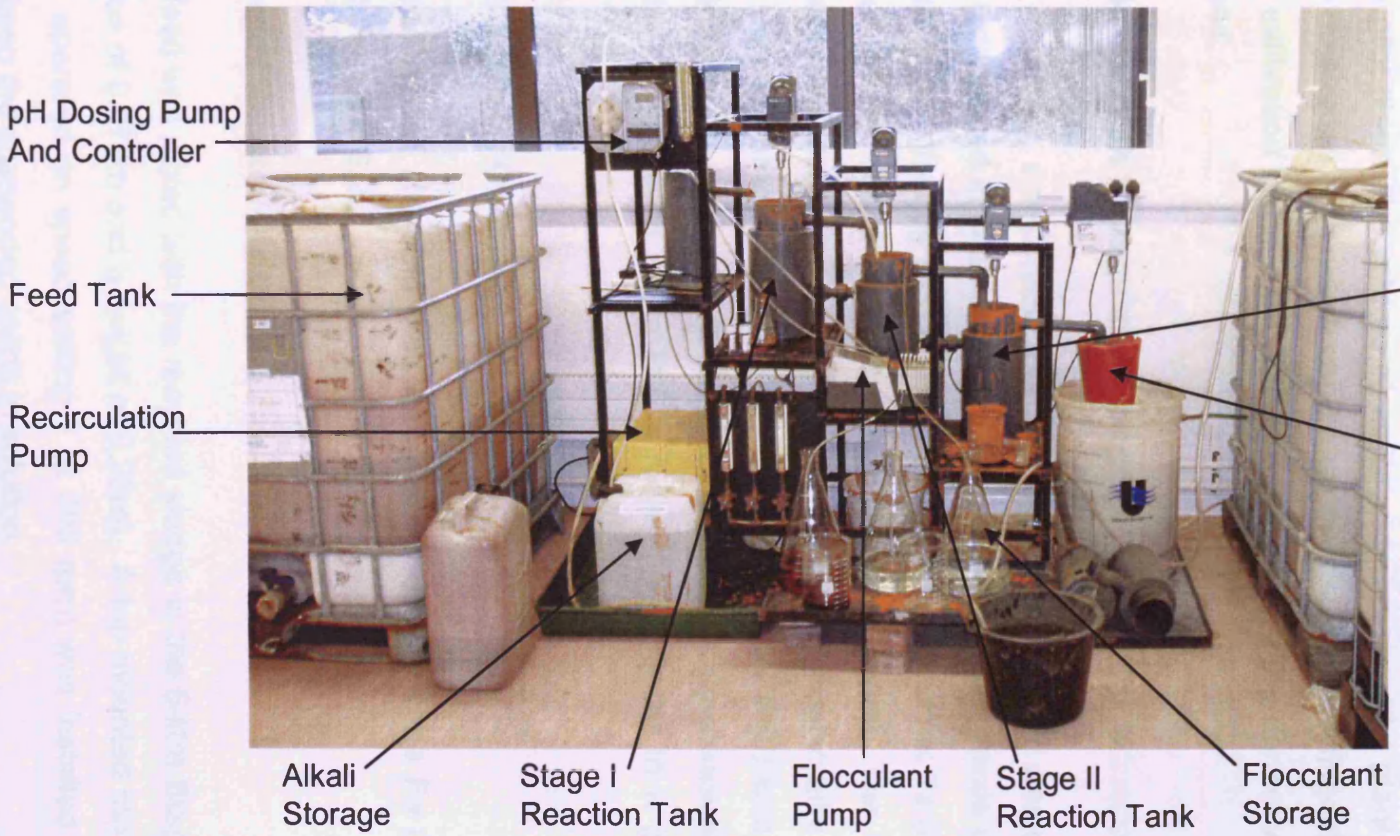


Figure 6.2: Photograph of the pilot plant

During the iron in seawater trial the seawater was collected twice a week from Sully Head, a point in the Severn Estuary, south west of Cardiff, and transported back to Cardiff University in a second IBC in a 'Pick-up' type van. The seawater was then pumped-over into the feed water reservoir IBC.

A water recirculation loop was used to ensure the IBC contents were fully mixed. A valve on the recirculation pumping line controlled the feed from the recirculation loop to the pilot plant. The volume of water added to the pilot plant each day was logged (by measuring the volume used from the IBC) and additionally, daily "drop" tests (flow calibration tests) were carried out to ensure the correct water feed rate was obtained.

6.2.2 Iron Solution Storage and Pumping

During the iron trials, a separate storage and pumping system was used to ensure the Fe (II) ions stayed in solution. Stock Fe (II) chloride was made up at 20 g/l (as iron) and fed to the plant by a peristaltic pump. When the stock Fe (II) chloride was refilled, the amount of Fe (II) chloride added was logged. The volume of the solution used was also recorded on a daily basis and additionally regular "drop" tests were carried out to ensure the correct feed rate of Fe (II) ions was obtained. (Pump drop tests or calibration tests were carried out by measuring the volume delivered by the iron feed pump into a measuring cylinder in a given 2 minute period.)

6.2.3 Feed Mixing Chamber

A 1-litre feed mixing chamber was installed for use with the Fe (II) addition as described in Section 6.2.2.

6.2.4 Stage I Reactor Vessel

The plant feed was mixed with the recycled sludge in the 5-litre Stage I (cylindrical with a radius of 0.075m and a height of 0.28m). A top mounted mixer (a Heidolph RZR 2041 operated on speed setting 1 at 293 rpm) was installed in the Stage I reactor to keep the suspended solids in solution.

6.2.5 Stage II Reactor Vessel

The overflow from the Stage I reactor was fed into the similarly sized Stage II

reactor, where the pH was raised by the addition of the alkali reagent. Air was introduced to ensure the full oxidation of the metals. A top mounted mixer (a Heidolph RZR 2041 operated on speed setting 1 at 200 rpm) was used to increase oxygen transfer rate and ensure adequate mixing.

6.2.6 Flocculation Tank

The treated water from the Stage II reactor overflowed into the Floc-Mixing Tank (volume 2.5litre, cylindrical with a radius of 0.075m and a height of 0.14m). Flocculant was added in two places: the first dosing point was the feed line from the Stage II reactor, and the second was directly into the flocculation tank. A slow-speed flocculation mixer (a Heidolph RZR 2041 operated on speed setting 1 at 139 rpm) was used for solids and flocculant mixing. The flocculated mixture then flowed via gravity into the clarifier.

6.2.7 Clarifier/Thickener Unit

Solids/liquid separation was achieved in a clarifier/thickener cone, with a maximum surface area of approximately 0.0176 m^2. Thickened solids from the clarifier were either recirculated to the Stage I reactor or excessed (removed) from the system from the base of the thickener via a peristaltic pump (Watson Marlow SciQ 323). The volume of sludge returned to the Stage I reactor was regularly monitored to ensure the correct recirculation sludge flow rate. The rate of removal of sludge was controlled to ensure the concentration of solids in the system was in the required operating range when possible. A slow-speed mixer (a Heidolph RZR 2041 operated on speed setting 1 at 76 rpm) was used to assist solids/liquid separation. Treated water was discharged from the system by overflowing the clarifier unit.

6.2.8 Alkali Reagent Dosing System

Alkali reagent was supplied from a storage vessel and dosed to the Stage II reactor via an integral controller/metering pump (Hanna Instruments BL 7916). The dosing rate was controlled via a pH probe located at the outlet of the Stage II reactor. The pH controller was calibrated twice a week to an accuracy of 0.2pH and the pH measurement was also checked by use of a Hanna Instruments HI9214 portable pH meter (also calibrated twice a week to an accuracy of 0.2pH). Should a difference of greater than 0.2pH be detected, both pH meters were

recalibrated. The pH controller was used to maintain the Stage II reactor pH appropriate for the metal in the feed water, with the pHs listed in Table 6.1.

During Trials 1 to 5, sodium hydroxide, which was stored in a 25 litre storage vessel, was used as the alkali reagent. The sodium hydroxide stock solution was made up to a strength of 10.2 g/l by dissolving 204 g of sodium hydroxide pellets in 1 litre of hot tap water, to ensure all the pellets dissolved, and then made up to 20 litres using tap water. Each day the volume added was recorded.

During Trial 6, calcium hydroxide was used as the alkali reagent, as this is the common alkali used during minewater treatment, and delivered to the plant from a 50 litre storage tank. Each day the 50 litre storage tank was filled with tap water and the volume of tap water added noted. For each litre of tap water, 6 g of calcium hydroxide powder was added, giving a stock calcium hydroxide solution of approximately 6 g/l.

Each day the alkali reagent storage vessel was filled and the volume of alkali reagent added was logged. When calcium hydroxide was used as the alkali reagent, an external pump and recirculation loop was used to ensure the calcium hydroxide storage tank contents were fully mixed.

6.2.9 Flocculant Make-up System

Anionic flocculant (either Magnafloc 155 or Magnafloc 10 supplied by Ciba Speciality Chemicals, Bradford, UK) was made up at a concentration of 0.05% w/v (i.e. 0.5g of active flocculant/l). Due to problems experienced with reliability of pumping such low volumes of flocculant, two pumps were used to ensure that, should one pump fail, there would not be a total failure of the flocculant dosing system. The dosing pumps used were a FA Hughes (DCL) and a Gilson Miniplus2 peristaltic pump.

The volume of flocculant added was logged on a regular basis and additional "drop" tests were carried out regularly to ensure the correct flocculant dosage rate was obtained.

6.2.10 Air Blower System

Air was supplied to the Stage II reactor for metal oxidation. The air was introduced via a diffuser ring located within the Stage II reactor. The airflow rate was not

recorded during the trials, however the airflow rate was initially set up to ensure adequate air was available to oxidize all metals in all trials. Air Flow rate was set at approximately 10 l/min.

6.3 Pilot Plant Performance Monitoring

The performance of the pilot plant was assessed by monitoring the following: volume of water treated, water quality (influent and effluent), reagent consumption and sludge settlement characteristics (settling velocity and settled sludge density). Additionally, samples of sludge were analyzed by XRD, scanning electron microscopy and micro electrophoresis. Finally, sludge samples were subjected to centrifuge and piston press dewatering trials.

6.4 Trial 1 – Iron in Tap Water

6.4.1 Trial 1 Introduction

The iron in tap water trial was run between the 19th September 2003 and 6th October 2003. Key stages during this trial were:

- 19th September 2003, plant set up and commissioning;
- 19th September 2003 to 30th September 2003, build up of sludge mass and development of desired operating conditions;
- 30th September 2003 to 6th October 2003, operation of the plant with HDS operating conditions.

For the trial the desired feed flow rate was 10 l/hour and an iron concentration of 200 mg/l of iron (delivered as Fe (II) chloride). During the trial, the volume of tap water added to the IBC was logged as was the amount of Fe (II) chloride solution used. A total of 4212 litres of water was added to the IBC in the 410 hours equating to an average calculated feed flow rate of 10.3 l/hr. During the trial, a total of 969 g of iron (delivered as Fe (II) chloride, see Section 6.4.2) was used, giving an average iron concentration of 230 mg of iron /litre of feed water.

6.4.2 Iron Storage and Pumping

During the iron in tap water trial, an iron storage and pumping system was used to ensure the iron, introduced as Fe (II) chloride, remained in solution. Stock Fe (II)

chloride was made up at 20 g/l of iron from 35% w/w Fe (II) chloride solution, purchased from Albion Chemicals, Swansea, UK, and fed to the plant by a peristaltic pump at approximately 100 ml/hr. The volume of iron solution added was logged when the iron feed solution was refilled and additional 'pump drop tests' were carried out to ensure the correct iron feed rate was obtained.

6.4.3 Plant Water Quality

During this trial, water quality samples of the influent and effluent water were taken to monitor the plant performance. Additional 'stage' samples were also taken to evaluate the sludge generation rate. These samples also indicated in which reactor the iron was being removed from solution. The results of the analysis of these samples are presented in Table 6.2. The analysis was undertaken by ICP with the methodology described in Section 3.2.2.

Table 6.2: Trial 1 water quality results – Total iron concentrations

Date	Feed stock (g/l)	Feed water (mg/l)	Reactor I (g/l)	Reactor I filtered (mg/l	Reactor II (g/l	Reactor II filtered (mg/l	Discharge (mg/l)	Effluent filtered (mg/l)
22 Sept 03	17.5 18.8	392 399	-	-	-	-	0.68	-
24 Sept 03	18.9	147	-	13.5	-	1.90	2.70	-
26 Sept 03	14.8	1,390	4.2		4.26		14.0	
06 Oct 03	18.6	191	5.9	3.6	5.59	0.83	1.73	1.17

The results of the analysis indicated that the iron in the influent mixing chamber fluctuated between 147 and 1395 mg/l. The measured iron concentration of 1,395 mg/l on the 26th September 2003 was likely to have been caused by either disturbing settled iron particles in inlet mixing chamber or analytical error, as the result is an order of magnitude too high. This same analytical methodology error could also explain the discharge iron concentration of 14 mg/l on the 26th September 2003.

Due to fluctuations in the measured iron concentration in the feed water, the trial average feed iron concentration was calculated by dividing the total iron load by the total water treated (see Section 6.4.1), giving an iron feed concentration of 230 mg/l. This value differs from the measured values (see Table 6.2), however this gives a more accurate iron loading onto the plant. The total iron added to the system (969 g) was also used to calculate the sodium hydroxide consumption

figure (see Section 6.4.6). Finally, to calculate the influent hydroxide load (see recirculation ratio, Section 6.4.12), the daily iron load was calculated and converted to an equivalent hydroxide value. This methodology was applied to all subsequent trials.

Presented in Table 6.2 are filtered Stage I reactor and Stage II reactor iron concentrations. These show that the majority of the iron was removed from solution in the Stage I reactor (91% on the 24th September 03 and 98% on the 6th October 2003). Table 6.2 also shows that on the 26th September 2003, iron accounted for 27% of the solids in the system (reactor solids concentration was 15.8 g/l), whilst on the 6th October 2003, iron accounted for only 20% of the solids (reactor solids concentration was 28 g/l).

Notional effluent quality targets were 1 mg/l for each metal, however due to poor settlement as a result of problems with the flocculant dosing system, occasionally the effluent metal concentrations were exceeded (as on the 26th September 2003).

Additional water samples were sent to a commercial laboratory (Wheal Jane Ltd Laboratories, Truro, Cornwall, UK) on the 6th October 2003 for further analysis. The results of the analysis undertaken by Wheal Jane Ltd are presented in Table 6.3.

Table 6.3: Trial 1 water and sludge quality (undertaken by Wheal Jane Ltd)

Determinand	Feed water (mg/l)	Discharge (mg/l)	Recycle sludge (g/l)	Flocculation tank contents (g/l)
Total solids	60.6	10.5	174	31.8
Total Sulphate	293	300	0.7	0.2
Total Calcium	45.1	18.1	4.9	1.0
Total Iron	163	0.18	97.2	18.2

The analysis undertaken at Wheal Jane Laboratories showed that there was no sulphate removed from the water (the difference in the sulphate concentrations can be explained by analytical error), approximately 60% of the calcium was removed and also confirmed the indicative iron concentrations. This analysis also showed that the iron accounted for 57% of the solids in the flocculation tank and 56% of the recycled solids. Assuming that the iron is removed as Fe (III) hydroxide ($Fe(OH)_3$), the theoretical iron concentration would be 52.3%, which is comparable to the 56% to 57% measured in the samples sent to the Wheal Jane

Laboratories (taking into account analytical error).

6.4.4 Plant Flows and Reactor Retention Time

For the iron in tap water trial, the volume of feed water treated was calculated by carrying out regular flow calibration checks and by using the rotameter on the feed line. However, due to problems with blockages in the feed line, the feed rate could vary. For subsequent trials, the daily volume of water used in the IBC was logged, which gave more accurate measurements, as this was a measurement of the actual volume of water that had been pumped out of the IBC and through the plant. To measure the recirculation flow, regular flow calibration checks ('drop tests') were performed. Though more reliable than the feed line, the recirculation line was also prone to blockages.

During this trial the recirculation pump was working close to its lower operating limit, i.e. at about 5% of its maximum delivery rate. A more suitably sized pump, i.e. operating in the middle of its operating range, would have been advantageous and would be recommended for future work to give more flexibility in recirculation flow range.

The plant feed and recirculation flows are presented in Figure 6.3. The average feed flow rate was 10.3 l/hr and the average recirculation flow rate was 6.4 l/hr.

Each day the total flow (the sum of the feed water and recirculated sludge) through the pilot plant reactors was calculated. Using the total plant flow (feed flow plus recirculation flow) through the Stage I reactor (or Stage II reactor), the individual reactor retention time during the iron in tap water trial was calculated and is presented in Figure 6.3. The individual reactor retention time varied between 14 and 25 minutes with the average being 18 minutes.

On the 22nd and 23rd September 2003, the individual reactor retention time increased due to the reduced feed of influent water, reduced to minimise carry over of solids from the clarifier.

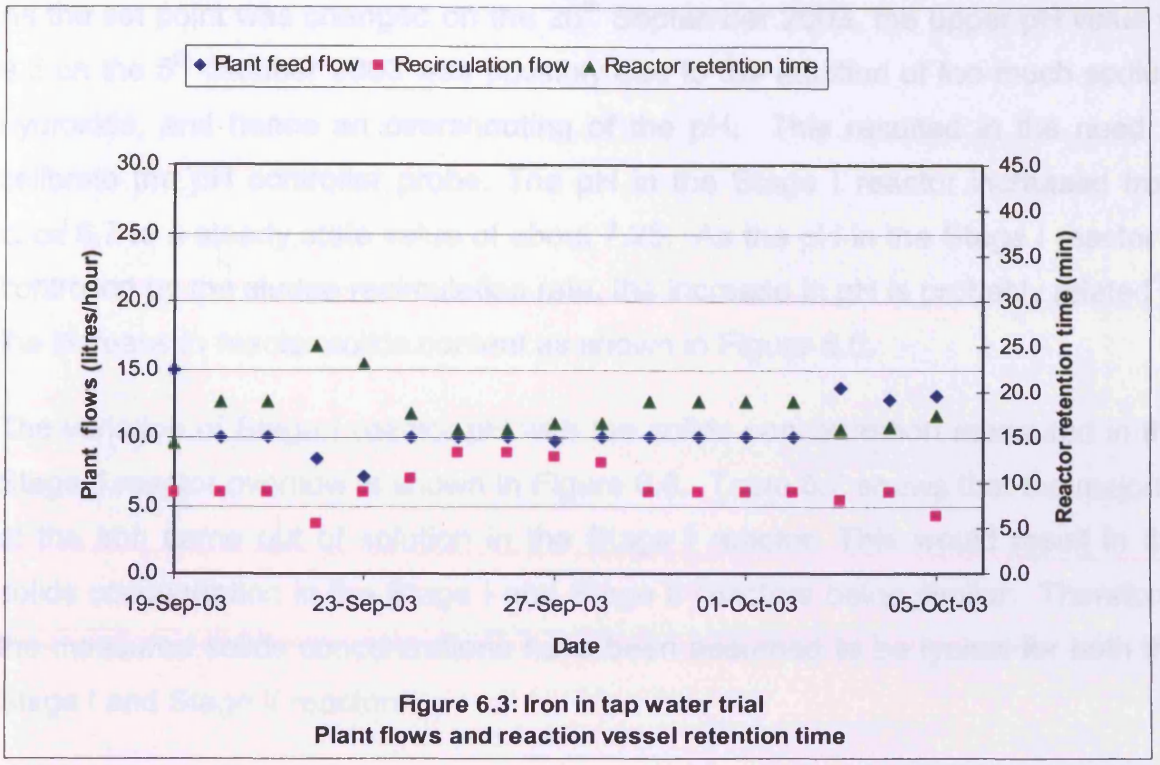


Figure 6.3: Iron in tap water trial
Plant flows and reaction vessel retention time

6.4.5 System pH, Redox Potential and Reactor Solids Concentration

Figure 6.4 indicates that the pH of the Stage II reactor varied during the set up and sludge build up period of the trial. However after the 27th September 2003, the pH remained approximately constant (varying between 9.2 and 9.6). The set-point in the pH controller was changed from 8.5 to 9.25 on the 26th September 2003.

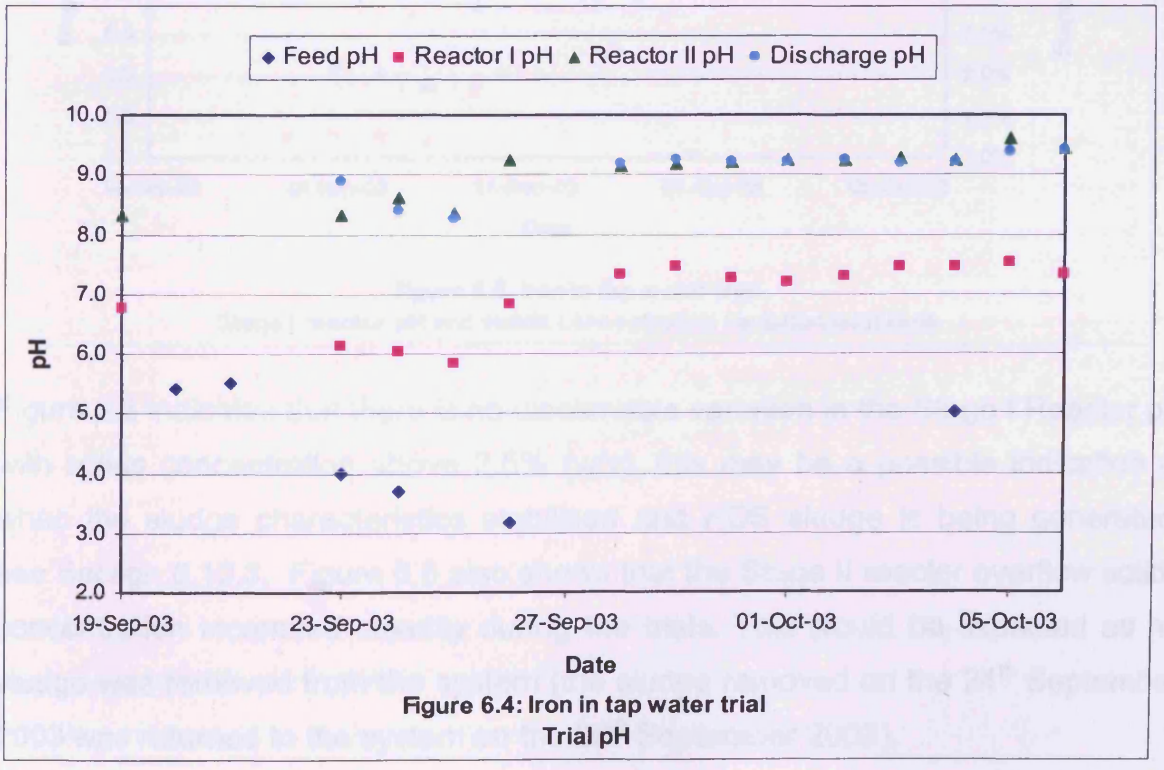


Figure 6.4: Iron in tap water trial
Trial pH

As the set point was changed on the 26th September 2003, the upper pH value of 9.6 on the 5th October 2003 was possibly due to the addition of too much sodium hydroxide, and hence an overshooting of the pH. This resulted in the need to calibrate the pH controller probe. The pH in the Stage I reactor increased from circa 6.7 to a steady state value of about 7.25. As the pH in the Stage I reactor is controlled by the sludge recirculation rate, the increase in pH is probably related to the increase in reactor solids content as shown in Figure 6.5.

The variation of Stage I reactor pH with the solids concentration measured in the Stage II reactor overflow is shown in Figure 6.6. Table 6.2 shows that the majority of the iron came out of solution in the Stage I reactor. This would result in the solids concentration in the Stage I and Stage II reactors being similar. Therefore, the measured solids concentrations have been assumed to be typical for both the Stage I and Stage II reactors.

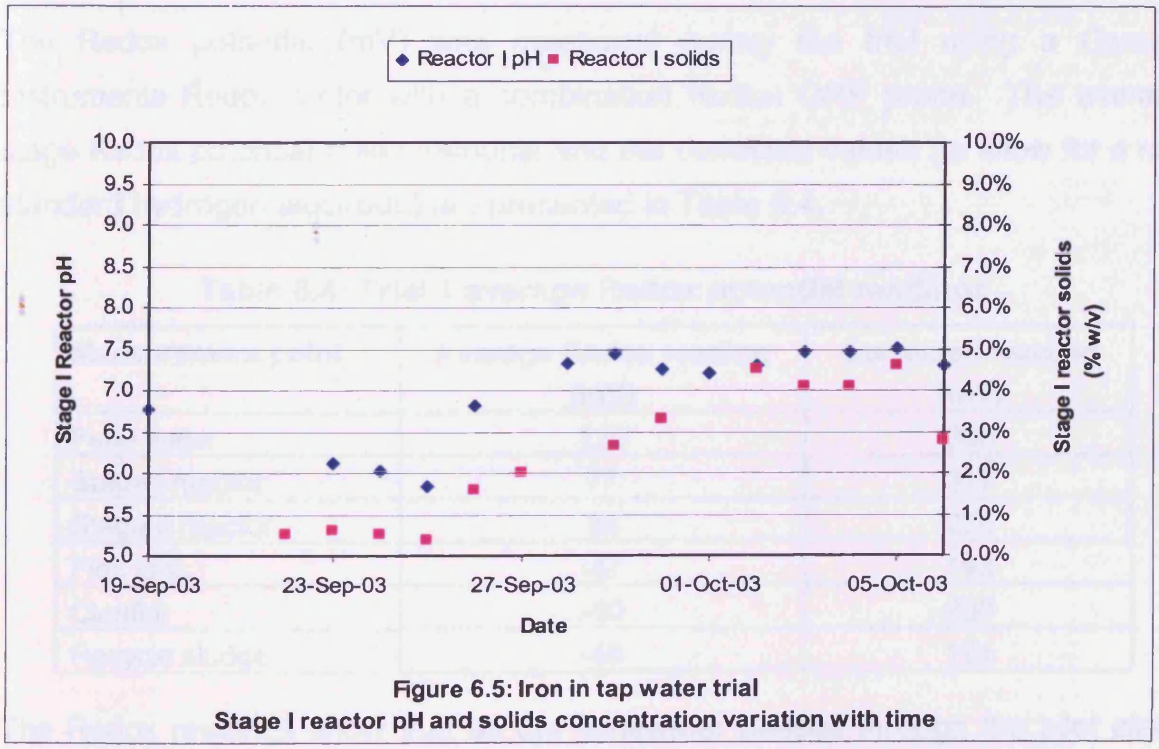


Figure 6.5: Iron in tap water trial
Stage I reactor pH and solids concentration variation with time

Figure 6.6 indicates that there is no discernable variation in the Stage I Reactor pH with solids concentration above 2.5% (w/v), this may be a possible indication of when the sludge characteristics stabilised and HDS sludge is being generated, see Section 6.10.3. Figure 6.6 also shows that the Stage II reactor overflow solids concentration increased steadily during the trials. This would be expected as no sludge was removed from the system (the sludge removed on the 24th September 2003 was returned to the system on the 26th September 2003).

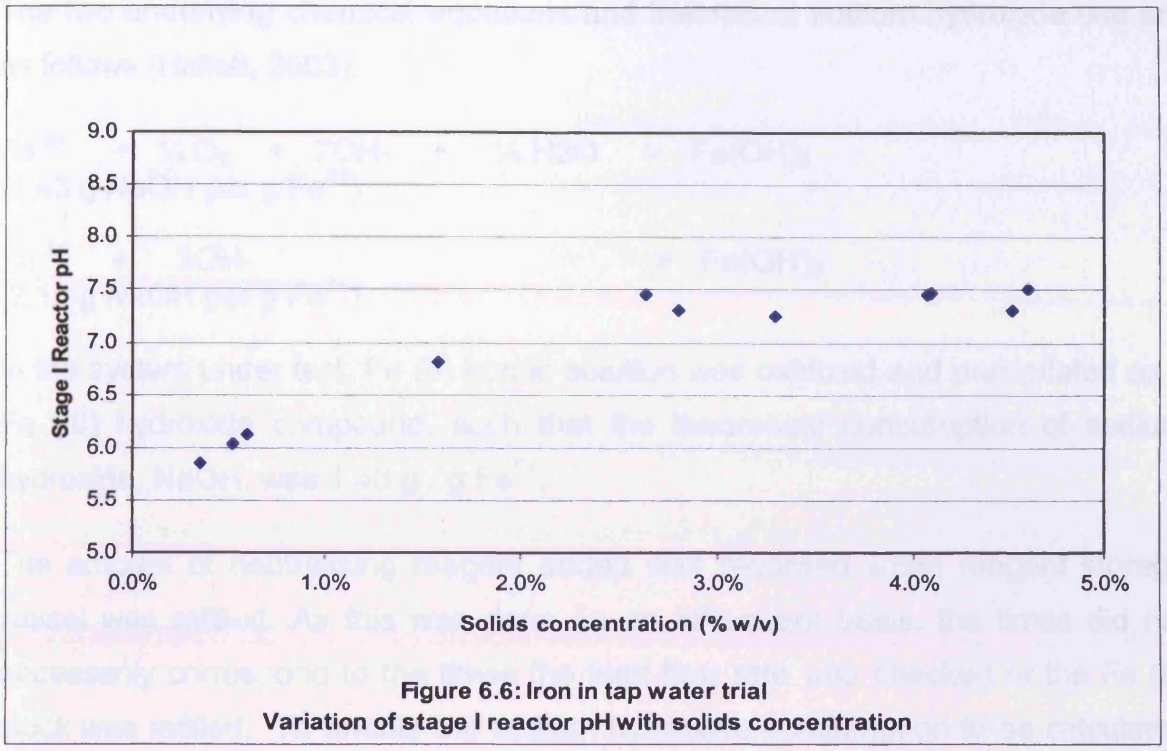


Figure 6.6: Iron in tap water trial
Variation of stage I reactor pH with solids concentration

The Redox potential (mV) was measured during the trial using a Corning Instruments Redox meter with a combination Redox ORP probe. The average stage Redox potential measurements and the corrected values (to allow for a non standard hydrogen electrode) are presented in Table 6.4.

Table 6.4: Trial 1 average Redox potential readings

Measurement point	Average Redox reading (mV)	Corrected reading (mV)
Feed water	120	360
Stage I reactor	77	317
Stage II reactor	34	274
Floc tank	-47	193
Clarifier	-40	200
Recycle sludge	-49	191

The Redox readings show that as the minewater passes through the pilot plant, the fluids become less oxidizing, as shown by the decrease in the Redox potential readings in the feed water and the clarifier contents.

6.4.6 Sodium Hydroxide Consumption

In view of the stoichiometry associated with dissolved Fe (II) iron being removed as either solid Fe (II) hydroxide or solid Fe (III) hydroxide, the theoretical values for reagent consumption and efficiency can be calculated.

The two underlying chemical equations and theoretical sodium hydroxide use are as follows (Hallett, 2003):

$Fe^{2+} + \frac{1}{4} O_2 + 2OH^- + \frac{1}{2} H2O > Fe(OH)_3$
(1.43 g NaOH per g Fe^{2+})

$Fe^{3+} + 3OH^- > Fe(OH)_3$
(2.15 g NaOH per g Fe^{3+})

In the system under test, Fe (II) iron in solution was oxidized and precipitated as a Fe (III) hydroxide compound, such that the theoretical consumption of sodium hydroxide, NaOH, was 1.43 g / g Fe^{2+}.

The amount of neutralising reagent added was recorded when reagent storage vessel was refilled. As this was done on an infrequent basis, the times did not necessarily correspond to the times the feed flow rate was checked or the Fe (II) stock was refilled. To enable the sodium hydroxide consumption to be calculated on a daily basis, the raw data was manipulated to produce daily usages for sodium hydroxide, Fe (II) ion added and water treated. The variation in the sodium hydroxide dose rate per gram of iron removed is shown in Figure 6.7.

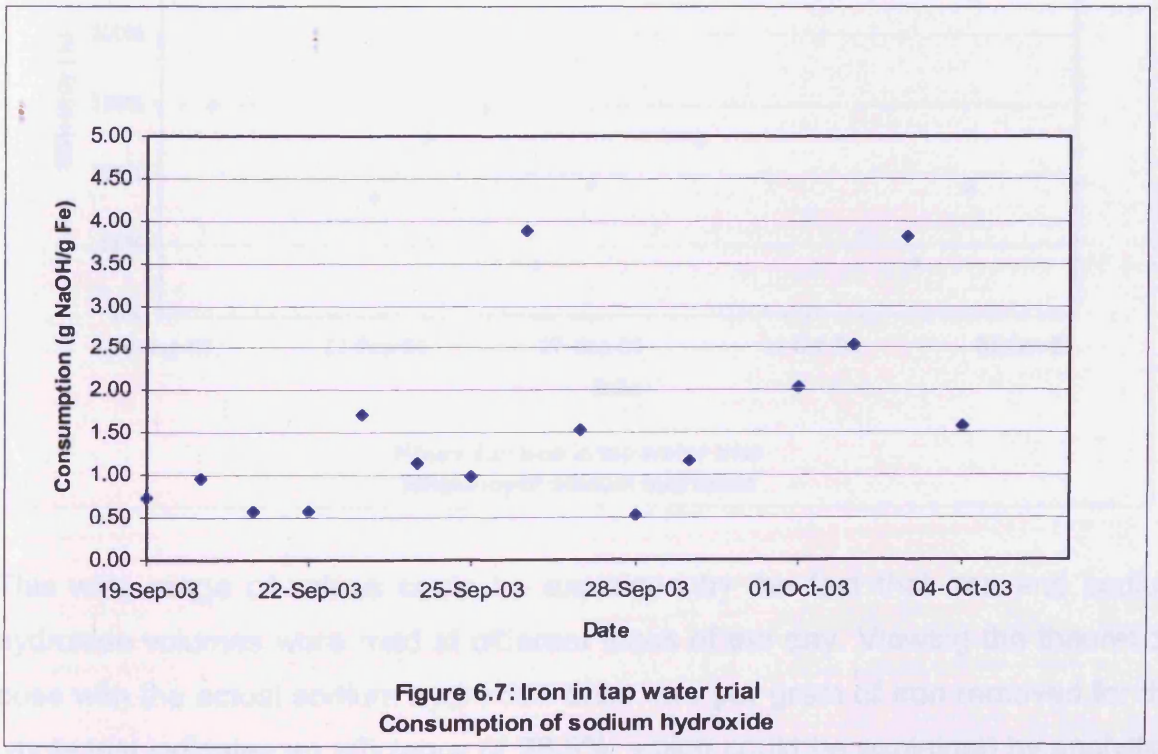


Figure 6.7: Iron in tap water trial
Consumption of sodium hydroxide

This reveals that the dose rate varied between 0.52gms and 3.88 g of NaOH per g of iron. The wide variation in consumption is likely to have been due to the fact that the reagent and iron readings were not taken at the same time. The average

dose was calculated by dividing the total weight of sodium hydroxide added during the trial (with the exception of the loads for the 30th September and 5th and 6th October 2003 as no measurement for the sodium hydroxide addition was recorded) by the total weight of Fe (II) ion added during the trial (again excluding the data for the 30th September 2003 and 5th and 6th October 2003). Given the total sodium hydroxide added was 1205g, and the total Fe (II) ion was 832g, the average dose was 1.45g of sodium hydroxide per g of iron removed, compared to theoretical values of 1.43g of sodium hydroxide per g of Fe (II) iron hydroxide. This is equivalent to a dose of 231 mg/l, using the total water treated of 3605 litres.

The variation in sodium hydroxide efficiency (in terms of theoretical/ actual dose required for Fe (II) iron precipitation) is shown in Figure 6.8 and varied between 37% and 276%.

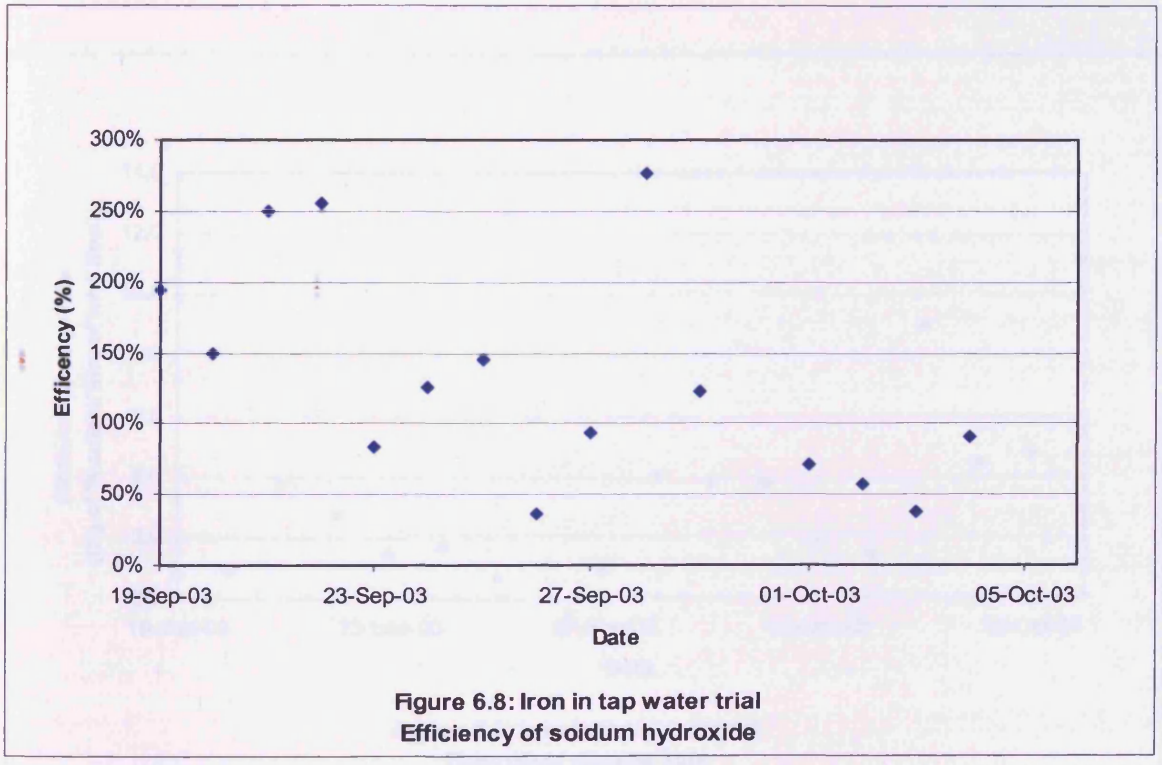


Figure 6.8: Iron in tap water trial
Efficiency of soidum hydroxide

This wide range of values could be explained by the fact that iron and sodium hydroxide volumes were read at different times of the day. Viewing the theoretical dose with the actual sodium hydroxide dose rate per gram of iron removed for the whole trial indicates an efficiency of 98.5%, which could be explained by analytical error. After the 30th September 2003, the sodium hydroxide usage stabilised and hence the sodium hydroxide efficiency stabilised. The wide variation in the apparent efficiency of sodium hydroxide can be misleading and only the average value based on total usages of the alkali reagent and target metal will be reported

for the subsequent trials.

6.4.7 Flocculant Consumption

The efficiency of the flocculant is greatly affected by a number of factors, including how the flocculant is added, the make-up concentration of flocculant and the sludge characteristics. The flocculant used during the trial was Magnafloc 155, supplied by Ciba Speciality Chemicals. On the 2nd October 2003, the flocculant addition was changed to a two stage dosing system. The flocculant was made up at a concentration of 0.05% w/v, 500mg of active flocculant /litre of water, and dosed at an average dose of 4.30 mg of active flocculant /litre of clarifier feed during the trial, and a total of 18.1 g used treating a total flow of 4212l in the trial. Figure 6.9 presents the flocculant dosage rates as mg of active flocculant per l of total flow to the clarifier.

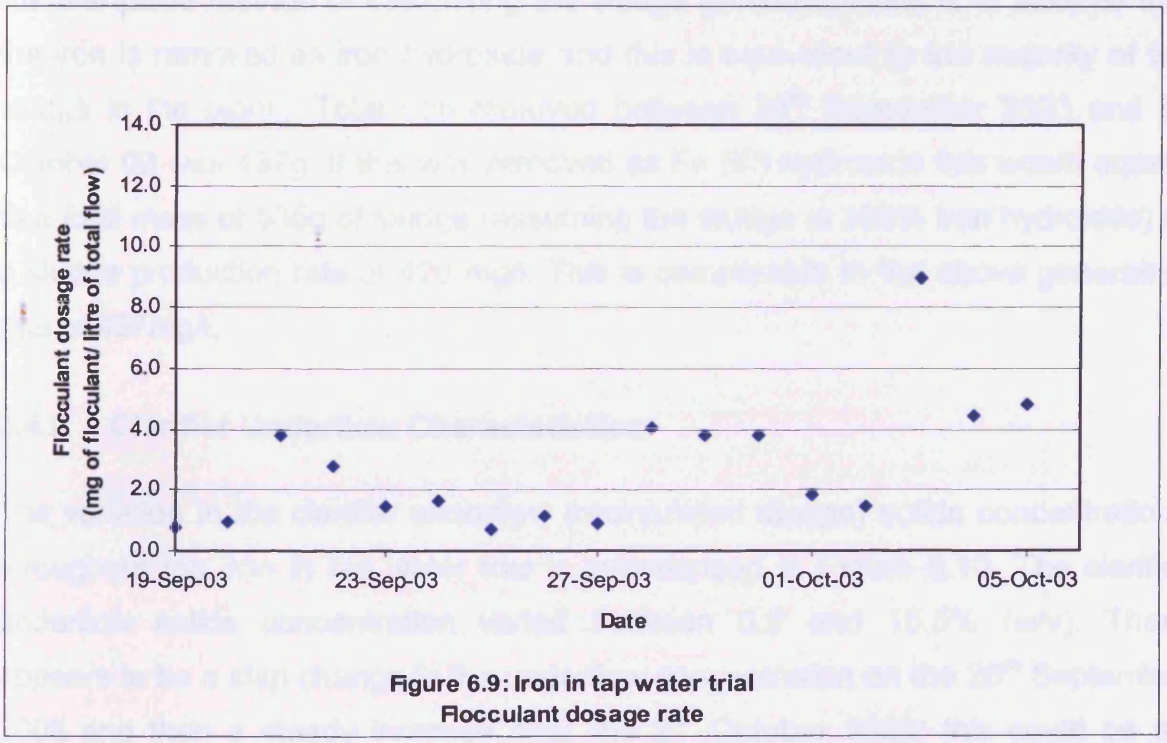


Figure 6.9: Iron in tap water trial
Flocculant dosage rate

Total flow to the clarifier was used instead of influent flow, which is the conventional method to calculate dosage rate, due to the occasional high rate of recirculation flow recorded. The wide range of flocculant dosage rates is an indication of an unstable system, which was not unexpected as all trials were designed to trial the various operating parameters, and once sludge stability was achieved the trials were stopped.

6.4.8 Sludge Generation Rate

The Stage I reactor solids concentration (presented in Figure 6.5) increased from 2.33% on the 28th September 2003 to 4.6% on the 5th October 03 and no solids were removed from the system (with the exception of the minimal amounts which were lost in the discharge water).

If all the iron was removed as Fe (III) hydroxide, the solids would theoretically contain 52.3% iron and this would equate to a solid generation rate of 1.91g of solids per g of iron removed. The results presented in Table 6.3 indicated, however, that 57% of the flocculation tank solids and 56% of the recycled sludge was iron, using an average value of 56.5% a solid generation rate of 1.77g of sludge per g of iron removed. Using an iron concentration of 230mg/l in the feed water, the sludge generation rate was 407mg/l.

An alternative method of calculating the sludge generation rate is to assume that the iron is removed as iron hydroxide and this is equivalent to the majority of the sludge in the plant. Total iron removed between 28th September 2003 and 5th October 03 was 437g. If this was removed as Fe (III) hydroxide this would equate to a total mass of 835g of sludge (assuming the sludge is 100% iron hydroxide) or a sludge production rate of 420 mg/l. This is comparable to the above generation rate of 407mg/l.

6.4.9 Clarifier Underflow Characteristics

The variation in the clarifier underflow (recirculated sludge) solids concentrations throughout the iron in tap water trial is summarised in Figure 6.10. The clarifier underflow solids concentration varied between 0.2 and 15.5% (w/v). There appears to be a step change in the underflow concentration on the 26th September 2003 and then a steady increase after the 2nd October 2003; this could be an indication of when HDS was produced. However, the solids concentration in the clarifier underflow was limited by the need to maintain a sufficiently high flow velocity through the recirculation pump to avoid blocking the pipe. The availability of a more suitably sized pump (see Section 6.4.4) would have allowed a lower recirculation flow rate to be used, which could have resulted in high clarifier underflow solids concentrations.

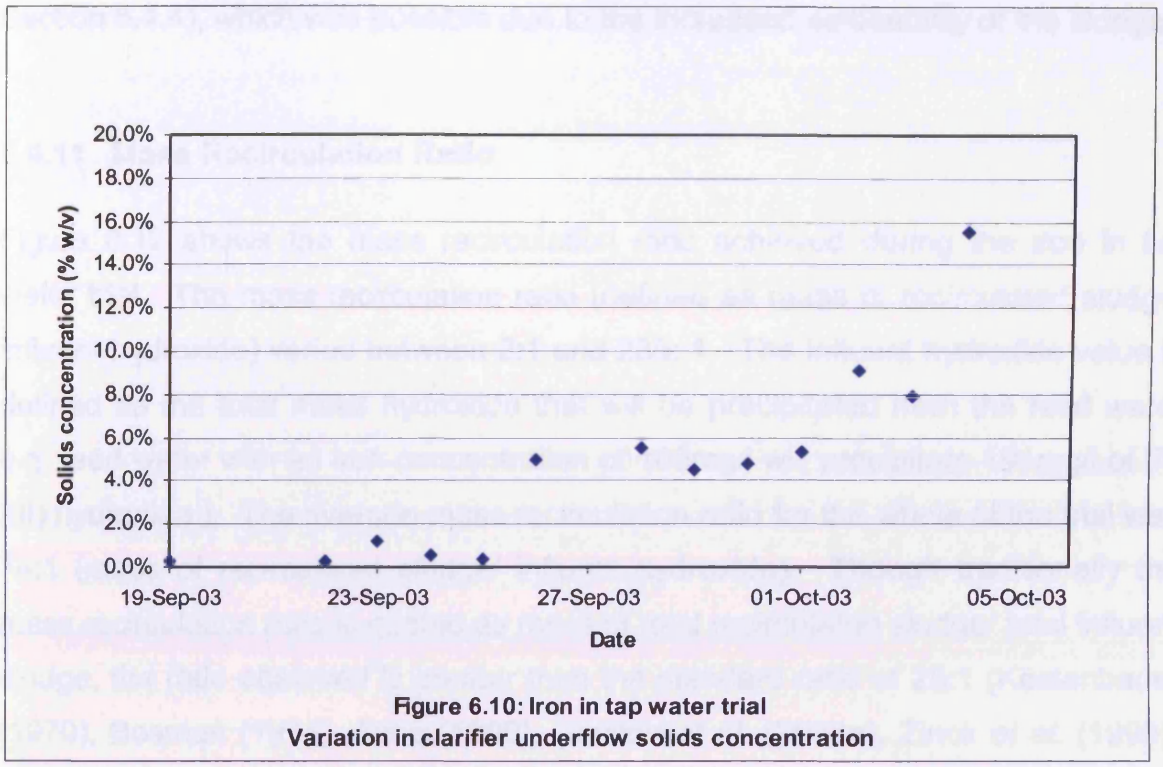


Figure 6.10: Iron in tap water trial
Variation in clarifier underflow solids concentration

6.4.10 Volumetric Recirculation Ratio

The variation of the volumetric recirculation ratio throughout the trial is shown in Figure 6.11.

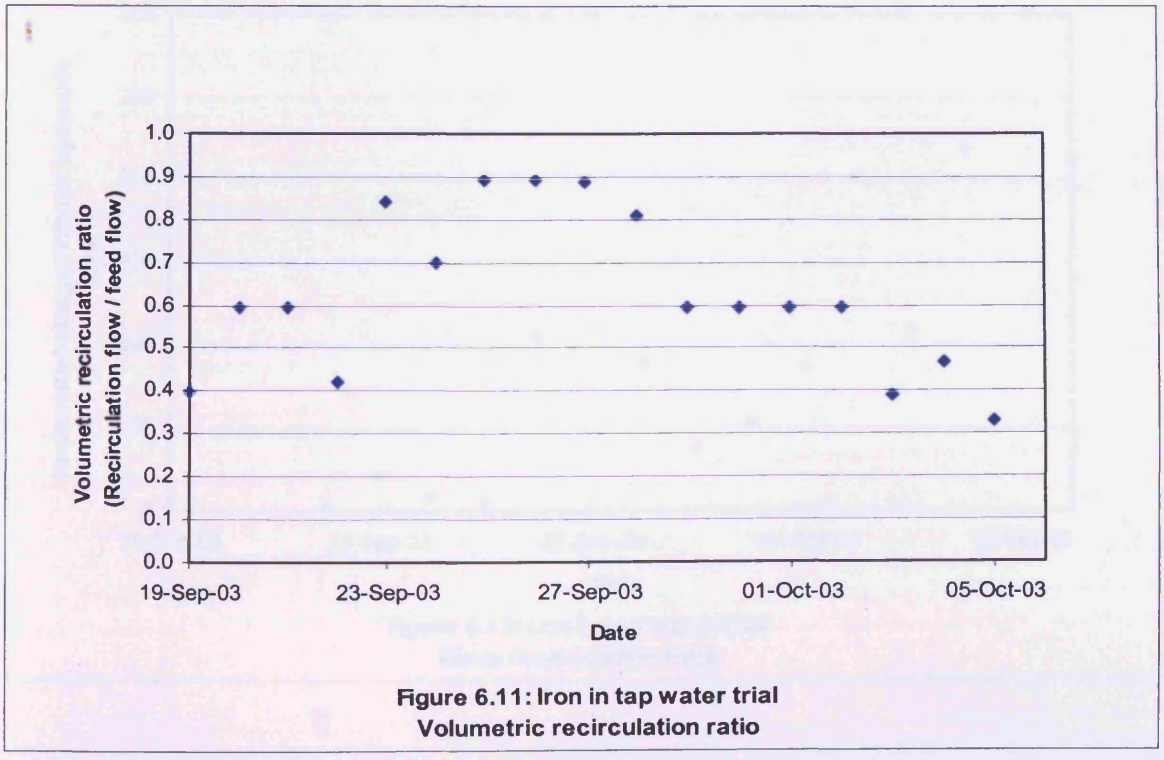


Figure 6.11: Iron in tap water trial
Volumetric recirculation ratio

The step changes in the reduction in the volumetric recirculation ratio on the 28th September and the 2nd October 03 were due to the increased feed flow rate (see

Section 6.4.4), which was possible due to the increased settleability of the sludge.

6.4.11 Mass Recirculation Ratio

Figure 6.12 shows the mass recirculation ratio achieved during the iron in tap water trial. The mass recirculation ratio (defined as mass of recirculated sludge/ influent hydroxide) varied between 2:1 and 235: 1. (The influent hydroxide value is defined as the total metal hydroxide that will be precipitated from the feed water e.g. feed water with an iron concentration of 100mg/l will precipitate 191mg/l of Fe (III) hydroxide.) The average mass recirculation ratio for the whole of the trial was 74:1 (mass of recirculated sludge/ influent hydroxide). Though traditionally the mass recirculation ratio is quoted as mass of total recirculated sludge/ total influent sludge, the ratio observed is greater than the standard ratio of 25:1 (Kostenbader (1970), Bosman (1974), Aube (1990), Coulton *et al.* (2003a), Zinck *et al.* (1999)) and was due to the fact that detailed analysis of the data did not occur until after the trial was complete. Constraints imposed by the sludge recirculation system in the plant also resulted in a higher mass recirculation ratio than desired.

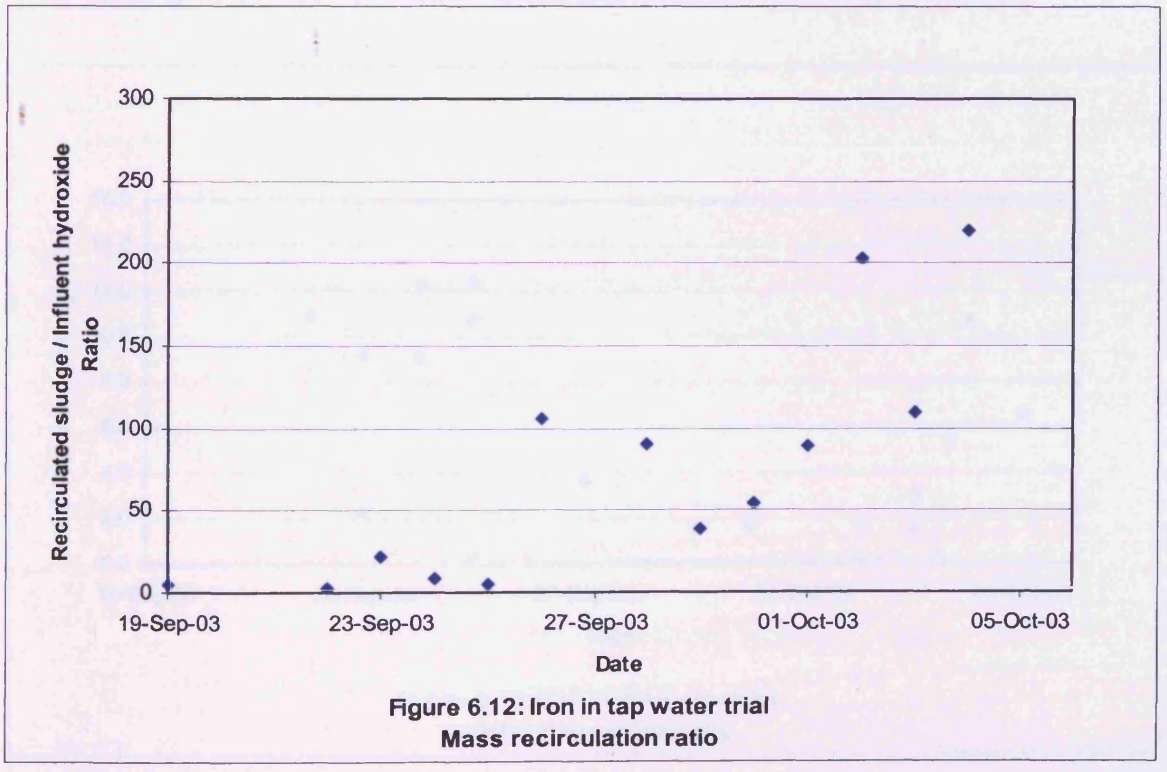


Figure 6.12: Iron in tap water trial Mass recirculation ratio

6.4.12 Sludge Settlement Characteristics

Settlement tests (sometimes called mudlines) were undertaken daily on the

flocculated slurry discharged from the Stage II reactor. Additional mudlines of recirculated and diluted flocculation tank sludge were also taken. The data derived from these tests have been used to calculate:

- The initial settling velocity (see Section 4.5.11)
- The final settled solids concentration (see Section 4.5.11)

6.4.13 Initial Settling Velocity

The measured initial settling velocities recorded for the iron in tap water trial are presented in Figure 6.13. This figure summarises the calculated initial settling velocities from the mudlines undertaken on diluted flocculation sludge, flocculation sludge and recycle sludge results. During the early part of the trail, the initial settling velocity was high. However, as the trial proceeded, the settlement velocity decreased due to the build up of solids causing hindered settlement. However, after the 2nd October 03 the settlement velocities increased to a maximum of 14.5 m/hr. This change in settlement characteristics on the 2nd October 03 could have been an indicator of the formation of high density sludge. During the whole trial the initial settling velocities recorded varied between 0.1m/hr and 14.5m/hr.

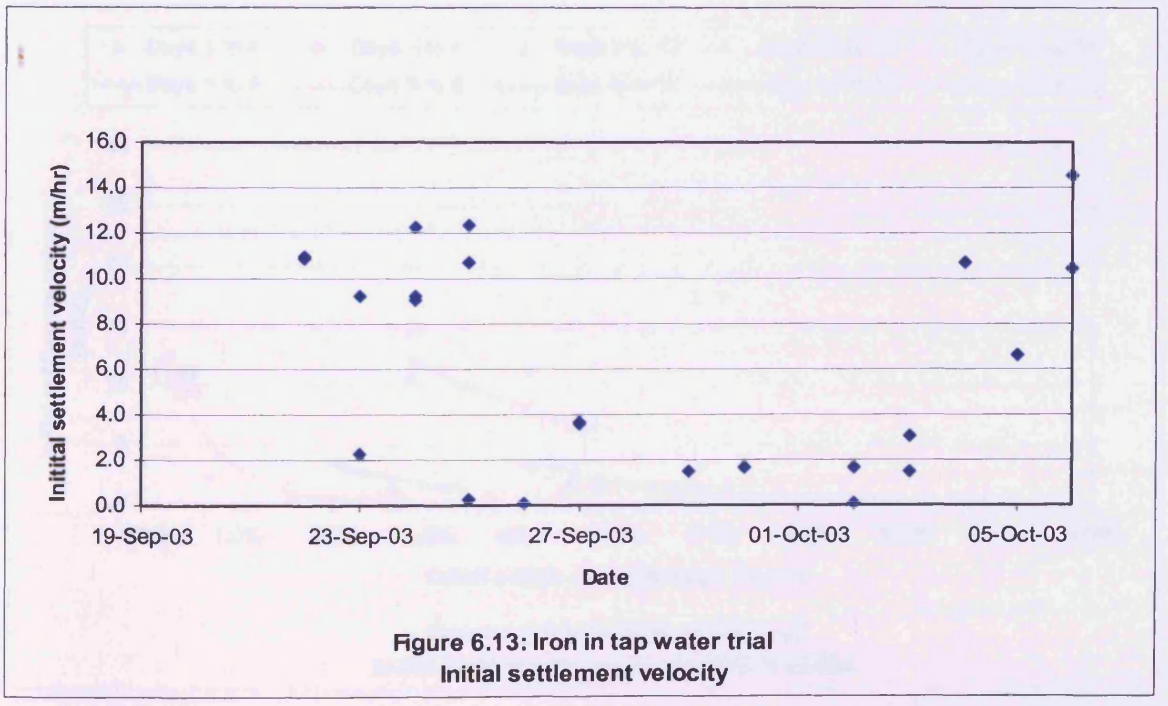


Figure 6.13: Iron in tap water trial
Initial settlement velocity

Figure 6.14, initial settling velocity and initial solids concentration, would appear to show that there is no discernable relationship between the initial solids concentration and the initial settling velocity.

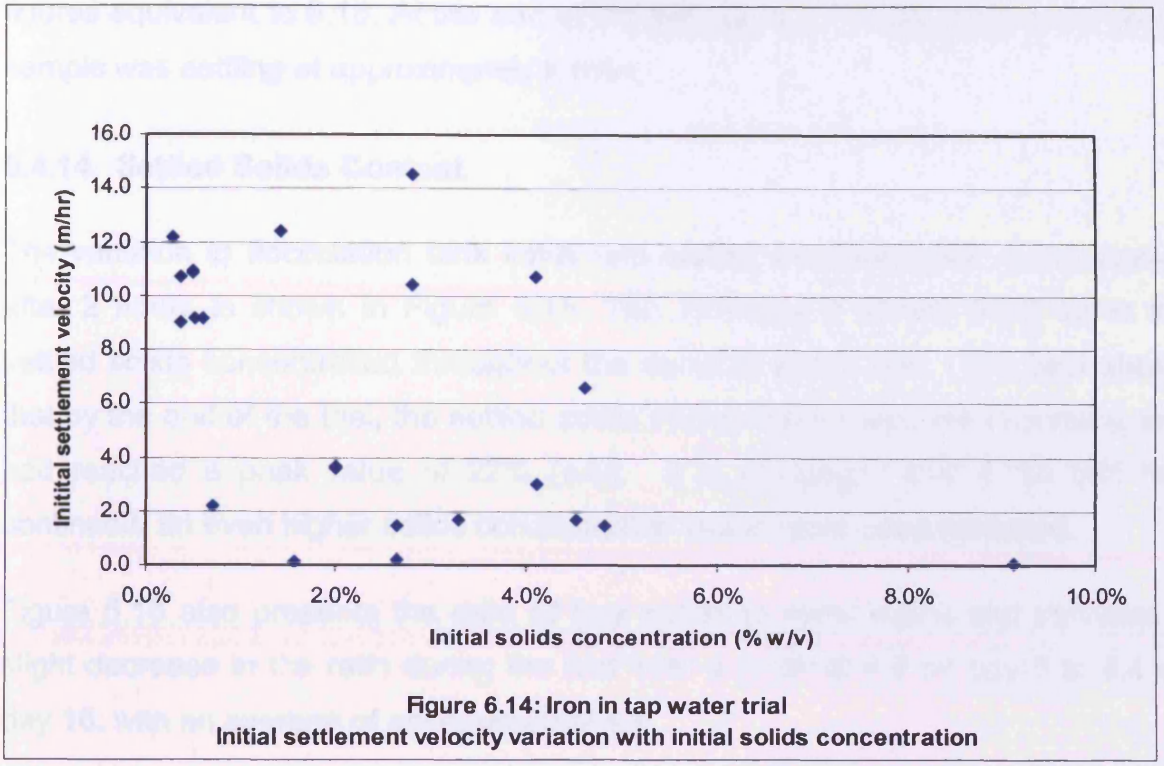


Figure 6.14: Iron in tap water trial
Initial settlement velocity variation with initial solids concentration

However, grouping the sludge by age enables the sludge age and concentration to be taken into consideration. Figure 6.15 presents the variation in initial settlement velocity with solids concentration in groups of 4 days.

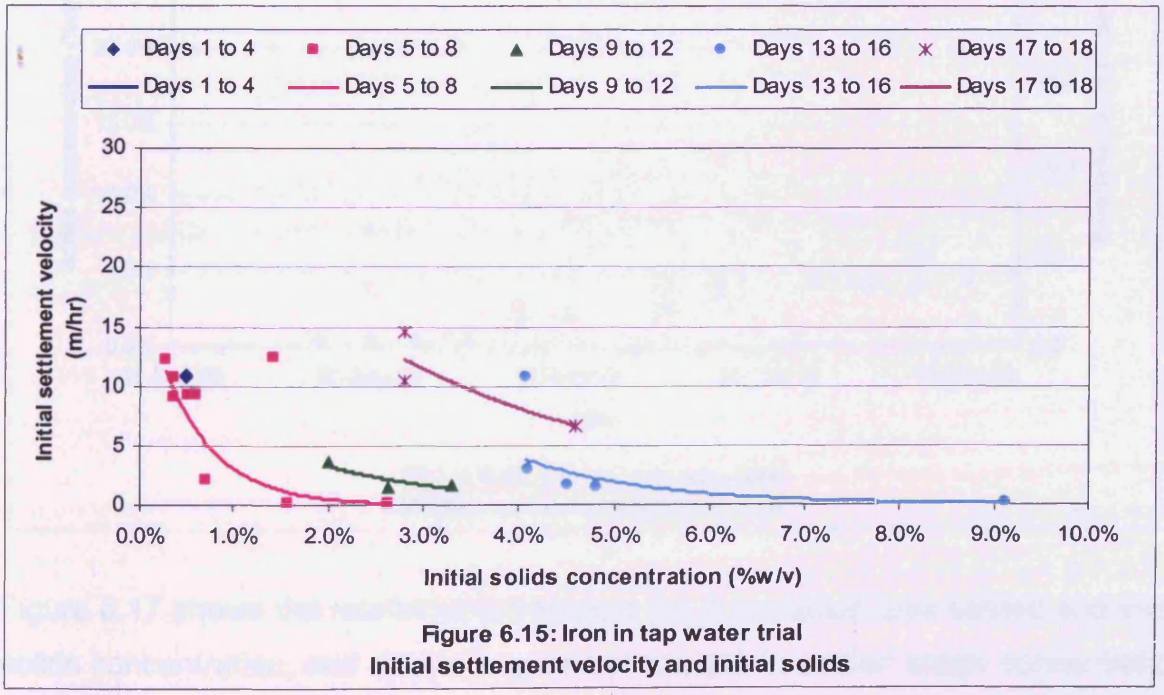


Figure 6.15: Iron in tap water trial
Initial settlement velocity and initial solids

This shows a general trend that as the sludge ages, the settlement velocity increases, i.e. the curves move from bottom left to top right. Hence we can omit Figures like 6.13 and 6.14 from all subsequent trial results and merely present

figures equivalent to 6.15. At the end of the trial, days 17 to 18, a 4% (w/v) solids sample was settling at approximately 8 m/hr.

6.4.14 Settled Solids Content

The variation in flocculation tank initial and settled mudline solids concentration after 2 hours is shown in Figure 6.16. This indicates a steady build up in the settled solids concentration throughout the duration of the trial. The data shows that by the end of the trial, the settled solids concentration was still increasing and had reached a peak value of 22% (w/v). It is envisaged that if the trial had continued, an even higher solids concentration would have been achieved.

Figure 6.16 also presents the ratio of final solids to initial solids and indicates a slight decrease in the ratio during the trial from a peak of 6.6 on day 5 to 5.4 on day 16, with an average of approximately 4.2.

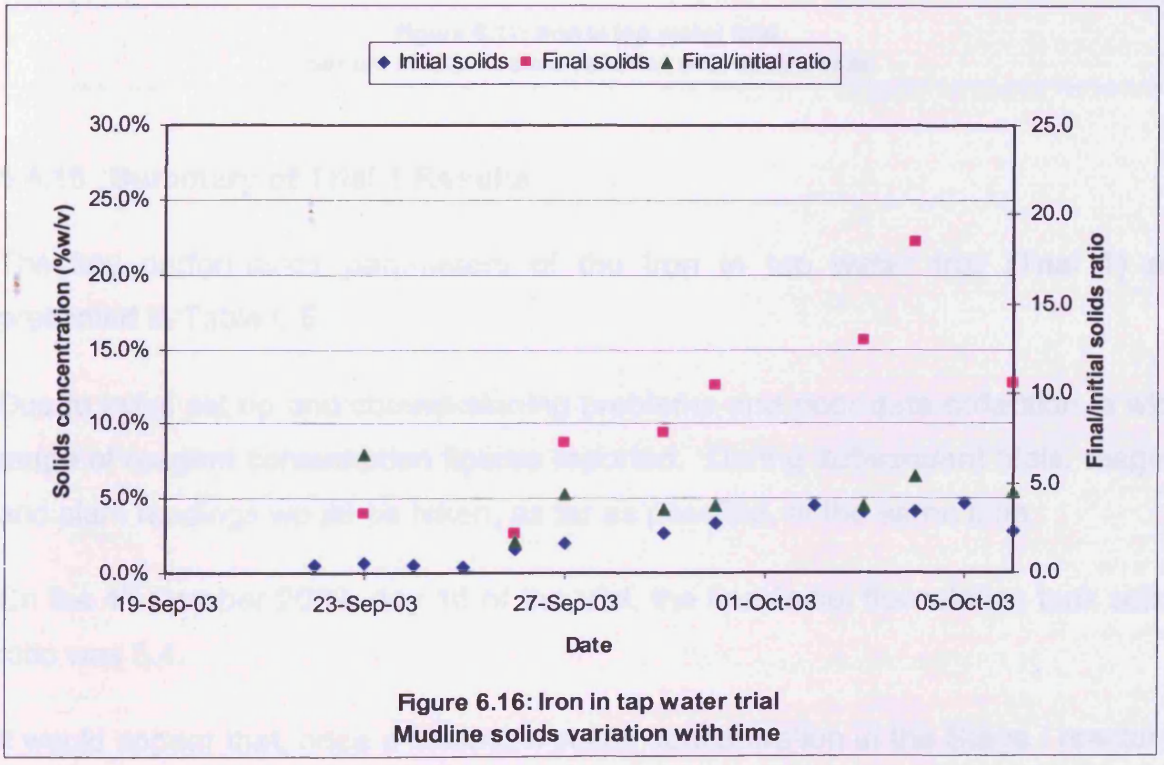


Figure 6.16: Iron in tap water trial
Mudline solids variation with time

Figure 6.17 shows the relationship between the flocculation tank settled and initial solids concentration, and shows a general increase in settled solids concentration with initial concentration. This is not surprising, due to the characteristics of the solids generated and shows for Trial 1 that there was approximately a linear relationship between initial solids and settled solids below an initial solids concentration of approximately 4.5 % (w/v). The slope of a linear trend line through

the data points in Figure 6.17 is approximately 4.7, which is similar to the final/initial solids ratio seen in Figure 6.16.

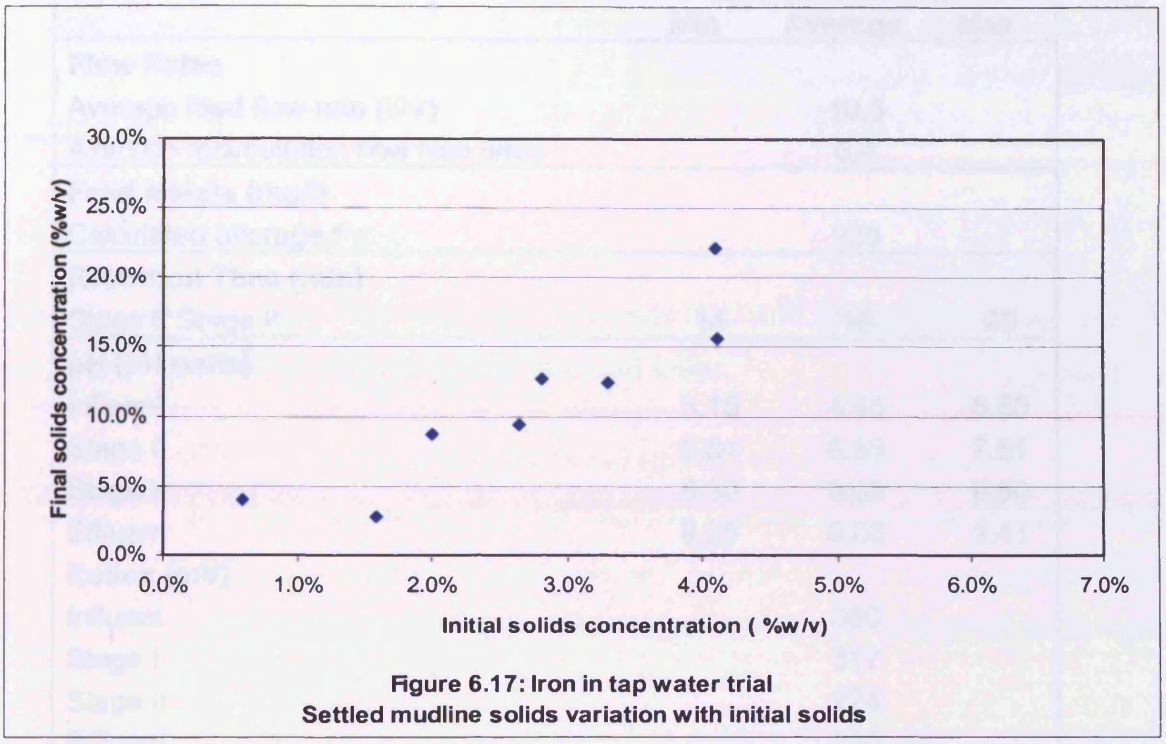


Figure 6.17: Iron in tap water trial
Settled mudline solids variation with initial solids

6.4.15 Summary of Trial 1 Results

The key performance parameters of the iron in tap water trial (Trial 1) are presented in Table 6.5.

Due to initial set up and commissioning problems and poor data collection, a wide range of reagent consumption figures reported. During subsequent trials, reagent and plant readings would be taken, as far as possible, at the same time.

On the 4th October 2003, day 16 of the trial, the final/initial flocculation tank solids ratio was 5.4.

It would appear that, once a minimum solids concentration in the Stage I reactor is achieved, the pH in that reactor is stabilised. In this trial, this occurred on about the 27th September 2003, when the solids concentration reached 2.5% (w/v) (Figure 6.4).

At the end of the trial, days 17 to 18, a 4% (w/v) solids sample was settling at approximately 8 m/hr.

On the 5th October 2003, day 17 of the trial, the initial settlement velocity showed

an increase in settlement rate. This could be an indication of the formation of HDS.

Table 6.5: Trial 1 key performance parameters

	Min	Average	Max
Flow Rates			
Average feed flow rate (l/hr)		10.3	
Average recirculation flow rate (l/hr)		6.4	
Feed Metals (mg/l)			
Calculated average Fe		230	
Retention Time (min)			
Stage I/ Stage II	14	18	25
pH (pH units)			
Influent	3.15	4.46	5.50
Stage I	5.84	6.99	7.51
Stage II	8.30	9.03	9.60
Effluent	8.25	9.06	9.41
Redox (mV)			
Influent		360	
Stage I		317	
Stage II		274	
Effluent		200	
Reagent Use			
Sodium hydroxide consumption (g/g)		1.45	
Sodium hydroxide consumption (mg/l)		231	
Sodium hydroxide efficiency (%)		98.5	
Flocculant dose (mg/l)		4.30	
Sludge Generation Rate (mg/l)		407	
Volumetric Recirculation Ratio	0.33	0.62	0.89
Mass Recirculation Ratio	2	74	236
Sludge Characteristics			
Reactor Solids (g/l)	3.60	24.3	46.0
2 Hour Settled Solids (g/l)	27.0	110	222
Recycle solids (g/l)	2.70	49.0	155
Initial settling Velocity (m/hr)	0.10	6.35	14.5
Final/ Initial solids ratio	1.71	4.23	6.58

A higher mass recirculation ratio than desired was used during the trial. This was primarily due to the inability to lower the recirculation pump speed, and compounded by the fact that the detailed review of the data did not take place until after the trial was complete.

Further analysis (e.g. XRD, SEM) and trials (e.g. centrifuge and piston press) were carried out on the sludge produced during the trial. These are presented in Chapter 7.

6.5 Trial 2 – Zinc in Tap Water

The results of the subsequent trials (Trials 2 to 6) are presented in the same way as 'Trial 1 – Iron in Tap Water' but eliminating certain plots as discussed. To limit repeated comments, the results are presented with summary comments where appropriate.

6.5.1 Trial 2 Introduction

The zinc in tap water trial was run between the 10th November 2003 and 28th November 2003. Key stages during this trial were:

- 10th November 2003, plant set up and commissioning;
- 11th November 2003 to 18th November 2003, build up of sludge mass and development of High Density Sludge (HDS) operating conditions;
- 19th November 2003 to 28th November 2003, operation of the plant with HDS operating conditions.

Zinc chloride powder, supplied by Fisher Chemicals, was added directly to an IBC of pH 7 tap water. During the period the 10th November 2003 to 13th November 2003, the pilot plant was fed at 95mg/l of zinc (delivered as zinc chloride) and increased on the 14th November 2003, to a concentration of 190mg/l. As with the iron in tap water trial, the desired feed flow rate was 10l/hour. The calculated feed flow rate was 9.78 l/hr with an average zinc concentration of 188mg of zinc /litre of feed water.

Due to problems with the blocking of the recirculated sludge line between 11th November and 18th November 2003, the pilot plant was run with sludge recirculating only during the working day (i.e. 8:00 to 18:00). The blockages resulted in no sludge being recirculated; this resulted in the sludge being 'carried over' from the clarifier in the discharge water. During the evenings and night-time (i.e. 18:00 to 8:00) of this period, the pilot plant was operated in conventional precipitation single pass mode. The operating pH of the Stage II reactor between 11th November 2003 and 18th November 2003 was 7.5, and for the remainder of the trial the operating pH was 8.5. After the 18th November 2003, the sludge characteristics improved sufficiently to allow the plant to be run continuously in HDS mode, i.e. with sludge recirculation flow, 24 hours a day. Plant Water Quality

Water quality samples of the influent and effluent water were taken during the trial.

These are presented in Table 6.6.

Table 6.6: Trial 2 water quality analysis – Total concentrations

Date	Determinand	Feed water (mg/l)	Filtered feed water (mg/l)	Filtered Reactor 1 (mg/l)	Filtered Reactor 2 (mg/l)	Discharge (mg/l)	Filtered effluent (mg/l)
27 Nov 03	Total Zinc	185	-	-	-	0.17	-
21 Nov 03	Total Zinc	190	-	-	-	0.24	-
28 Nov 03	Total Zinc	215	183	1.3	3.1	8.10	7.5
	Total Iron	0.1	0.1	0.1	0.1	0.10	0.1
	Total Calcium	46.6	53.8	96.3	50.6	47.4	58.0

Samples on 28 November 2003 were analysed after two months.

It is unsure why the effluent sample taken on the 28th November 2003 had a high zinc concentration of 8.1mg/l; this may have been due to a low pH.

6.5.2 Plant Flows and Reactor Retention Time

The plant feed and recirculation flow rates are presented in Figure 6.18.

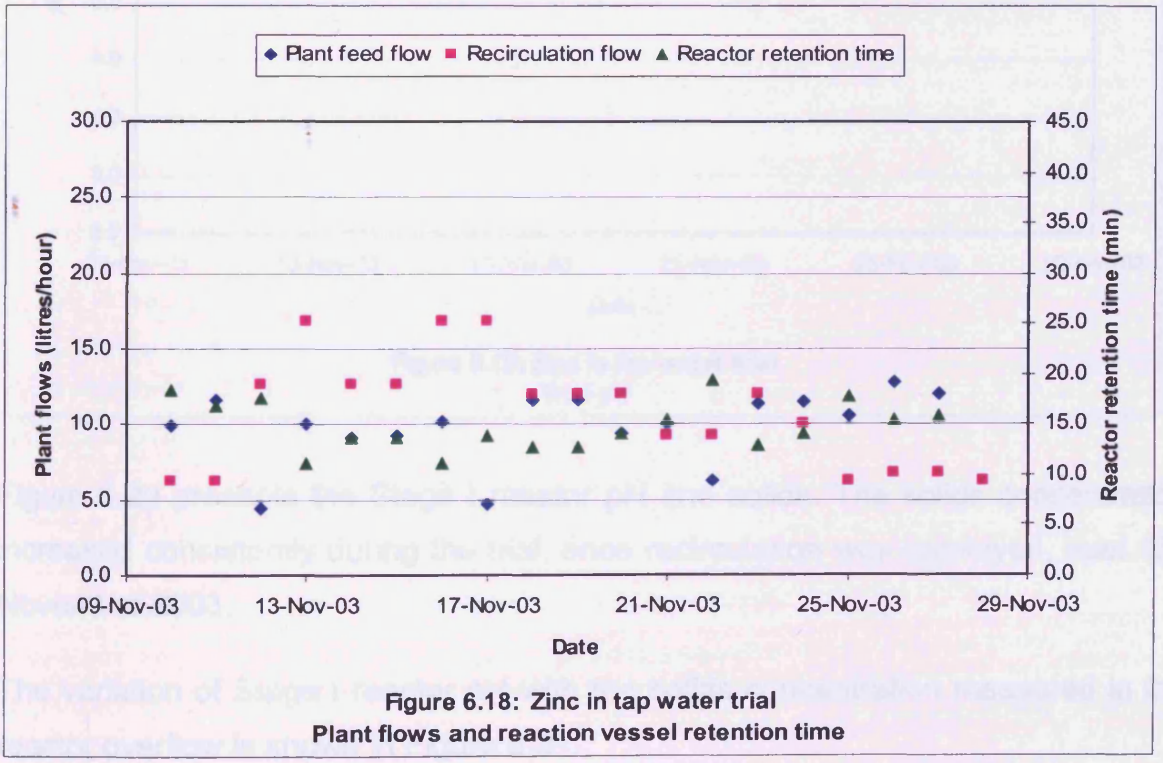


Figure 6.18: Zinc in tap water trial
Plant flows and reaction vessel retention time

For the whole of the trial the average feed rate during the trial was 9.8 l/hr whilst the recirculation flow rate averaged 10.7 l/hr. After the 18th November 2003, the average recirculation flow was 9.0 l/hr. The reactor retention time during the zinc in tap water trial is present in Figure 6.18 and varied between 11.1 and 19.3 minutes, with an average of 15.3 minutes.

6.5.3 System pH, Redox Potential and Reactor Solids Concentration

The variation in feed water, Stage I reactor, Stage II reactor and discharge pH throughout the zinc trial, are summarised in Figure 6.19.

Figure 6.19 indicates that the pH in both Stage I and Stage II reactors increased on the 18th November 2003; this corresponds to when the plant was cleaned out and all settlement put back into suspension. Post 18th November 2003, when the plant was run with recirculation flow, the Stage I pH averaged 8.3 (max 8.6 and min 7.8).

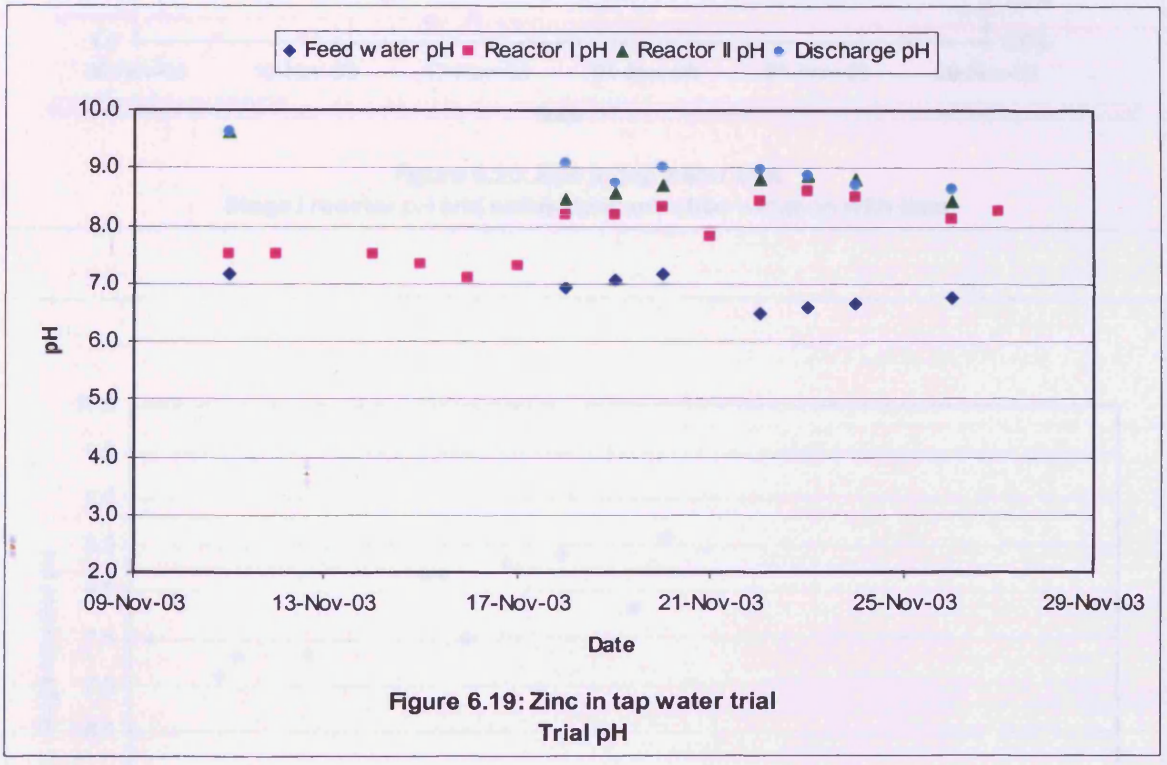


Figure 6.19: Zinc in tap water trial
Trial pH

Figure 6.20 presents the Stage I reactor pH and solids. The solids concentration increased consistently during the trial, once recirculation was employed, post 18th November 2003.

The variation of Stage I reactor pH with the solids concentration measured in the reactor overflow is shown in Figure 6.21.

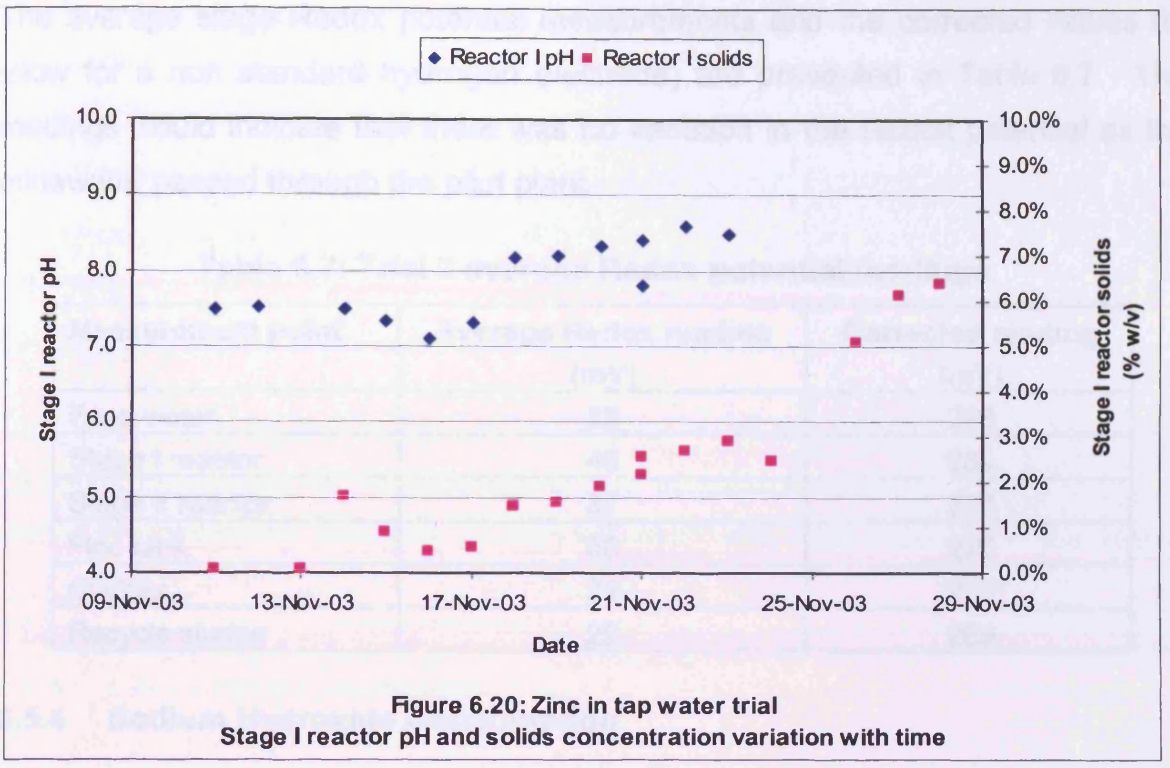


Figure 6.20: Zinc in tap water trial
Stage I reactor pH and solids concentration variation with time

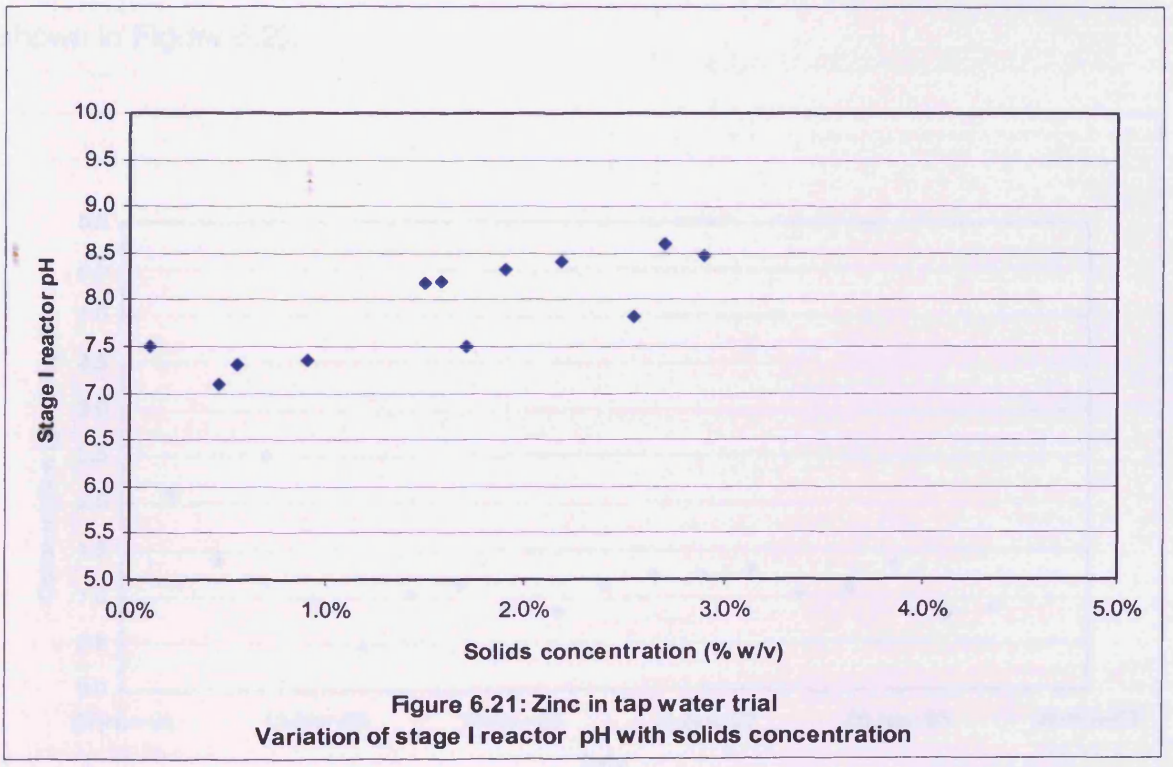


Figure 6.21: Zinc in tap water trial
Variation of stage I reactor pH with solids concentration

Figure 6.21 shows that, as the solids concentration increased, there was a corresponding rise in the Stage I reactor pH. It would appear that a Stage I reactor solids concentration of approximately 1.5% (w/v) was required to maintain a stable pH, however due to the change in the operating pH on the 18th November 2003, the exact point is a little uncertain.

The average stage Redox potential measurements and the corrected values (to allow for a non standard hydrogen electrode) are presented in Table 6.7. The readings would indicate that there was no variation in the Redox potential as the minewater passed through the pilot plant.

Table 6.7: Trial 2 average Redox potential readings

Measurement point	Average Redox reading (mV)	Corrected reading (mV)
Feed water	28	268
Stage I reactor	48	288
Stage II reactor	37	277
Floc tank	30	270
Clarifier	29	270
Recycle sludge	29	269

6.5.4 Sodium Hydroxide Consumption

The variation in the sodium hydroxide dose rate per gram of zinc removed is shown in Figure 6.22.

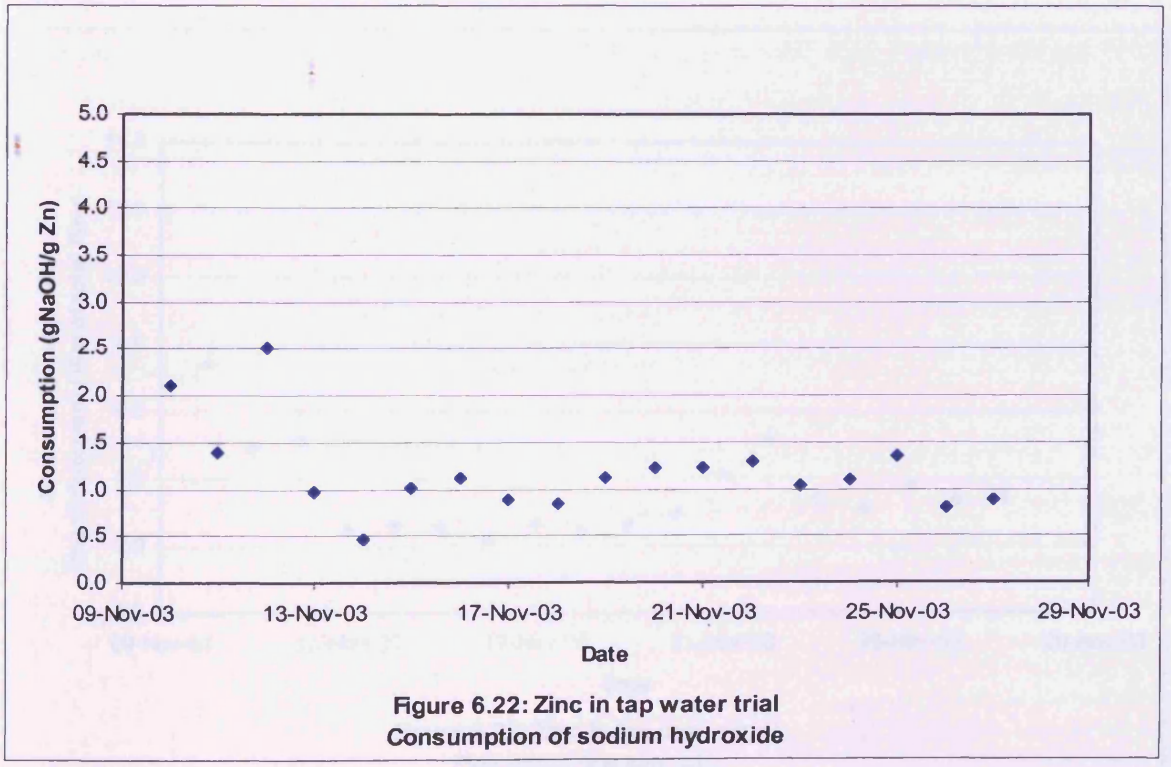


Figure 6.22: Zinc in tap water trial
Consumption of sodium hydroxide

The set-point in the pH controller was changed from 7.5 to 8.5 on the 18th November 2003. This shows that the dose rate varied between 0.46 g of sodium hydroxide per g of zinc and 2.52 g of sodium hydroxide per g of zinc. As previously indicated in Section 6.4.6, the preferred method of calculating the dose rate is to

look at the total amount of metal removed and the total amount of sodium hydroxide used during each trial. The total sodium hydroxide used during Trial 2 was 856.8 g and the total zinc removed was 790.4 g, equating to a dose rate of 1.08 g of sodium hydroxide per g of zinc, compared to theoretical values of 1.22g of sodium hydroxide per g of zinc hydroxide. This equates to a dose of 205 mg/l. The range of sodium hydroxide consumption was narrower than during Trial 1 and was possibly due to improved monitoring of the plant.

The sodium hydroxide efficiency (in terms of actual dose/ theoretical dose required for zinc precipitation) for the whole trial was calculated at 113%. Though this is a higher than expected efficiency (a high efficiency was expected due to the lack of pollutants in the feed water) it is still within experimental error.

6.5.5 Flocculant Consumption

During the zinc in tap water trial, the chosen flocculant, Magnafloc 10 (supplied by Ciba Specialist Chemicals), was dosed at an average flocculant dosage rate of 3.43mg/l. Figure 6.23 presents the daily dosage rates during the trial.

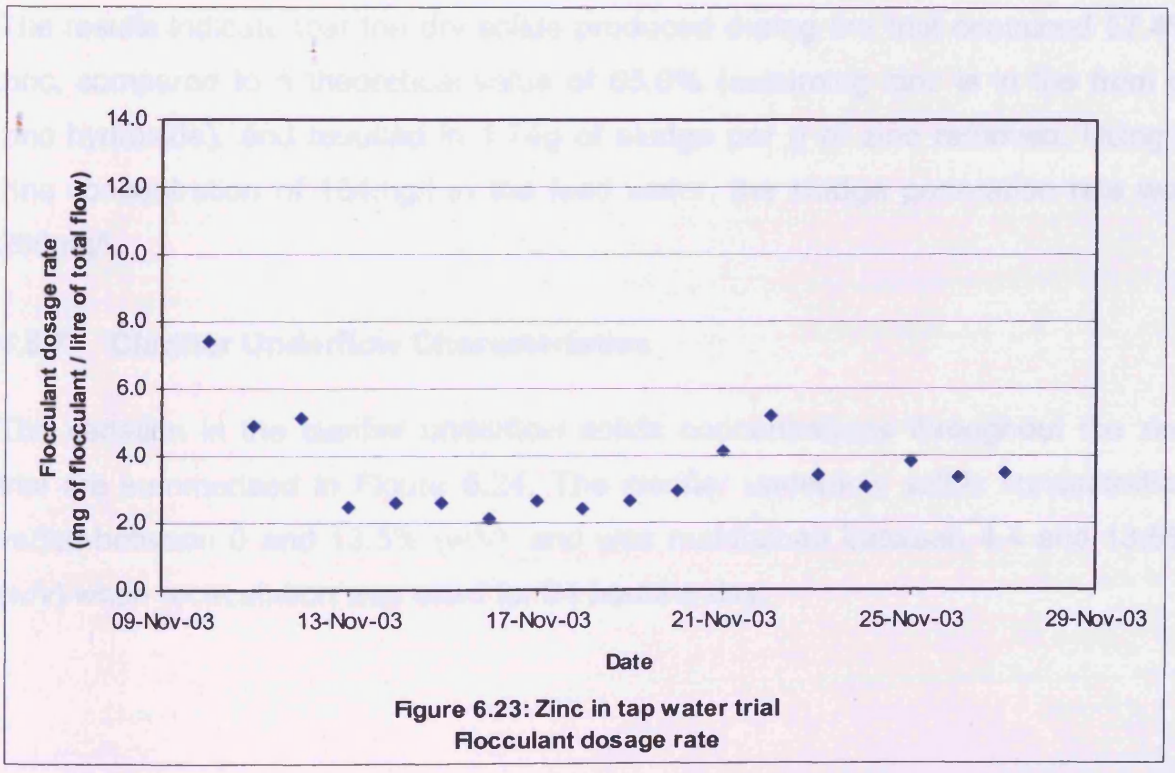


Figure 6.23: Zinc in tap water trial
Flocculant dosage rate

6.5.6 Sludge Generation Rate

To calculate the sludge generation rate during the zinc in tap water trial, analysis of the sludge was undertaken. Knowing the zinc content as a percentage of total

solids, and the zinc concentration in the feed water, the sludge generation rate can be calculated. Results of analysis of the sludge samples taken throughout the zinc trial are presented in Table 6.8.

Table 6.8: Trial 2 sludge dry solids composition (% of total solids)

Date	Zn %	Fe %	Si %	Ca %	Al %	$Fe(OH)_3$ %	$Zn(OH)_2$ %	$CaCO_3$ %	$Al(OH)_3$ %
14 Nov 03	51.5	0.8	0.5	0.7	0.0	1.5	78.5	1.8	0.1
15 Nov 03	51.1	1.0	0.4	0.6	0.0	2.0	77.8	1.4	0.1
17 Nov 03	56.6	0.9	0.4	0.4	0.0	1.8	86.2	1.0	0.1
18 Nov 03	56.6	1.0	0.4	0.6	0.0	1.9	86.2	1.4	0.1
19 Nov 03	60.0	0.8	0.4	0.3	0.0	1.5	91.4	0.7	0.1
20 Nov 03	58.7	0.7	0.4	0.5	0.0	1.4	89.5	1.1	0.1
21 Nov 03	59.4	0.6	0.4	0.5	0.0	1.1	90.4	1.3	0.1
22 Nov 03	57.7	0.5	0.4	0.4	0.0	1.0	87.9	0.9	0.1
23 Nov 03	57.7	0.5	0.4	0.4	0.0	1.0	87.9	1.1	0.1
24 Nov 03	56.0	0.4	0.4	0.4	0.0	0.8	85.3	1.0	0.0
25 Nov 03	60.1	0.5	0.4	0.3	0.0	0.9	91.5	0.7	0.1
26 Nov 03	60.1	0.5	0.4	0.4	0.0	0.9	91.5	1.1	0.1
27 Nov 03	60.2	0.4	0.4	0.4	0.0	0.7	91.6	1.0	0.0
Average	57.4	0.7	0.4	0.4	0.0	1.3	87.1	1.2	0.1

The results indicate that the dry solids produced during the trial contained 57.4% zinc, compared to a theoretical value of 65.6% (assuming zinc is in the from of zinc hydroxide), and resulted in 1.74g of sludge per g of zinc removed. Using a zinc concentration of 154mg/l in the feed water, the sludge generation rate was 268mg/l.

6.5.7 Clarifier Underflow Characteristics

The variation in the clarifier underflow solids concentrations throughout the zinc trial are summarised in Figure 6.24. The clarifier underflow solids concentration varied between 0 and 13.5% (w/v), and was maintained between 4.4 and 13.5% (w/v) when recirculation was used for 24 hours a day.

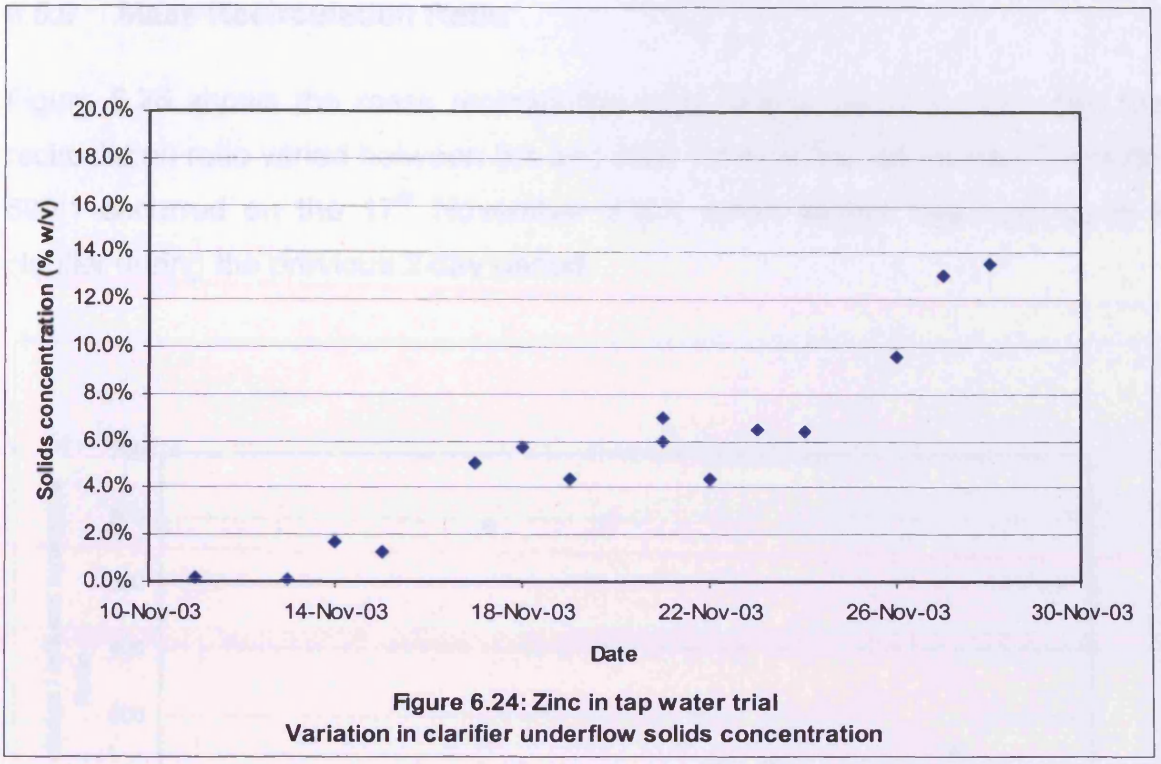


Figure 6.24: Zinc in tap water trial
Variation in clarifier underflow solids concentration

6.5.8 Volumetric Recirculation Ratio

The variations of the volumetric recirculation ratio throughout the zinc trial are shown in Figure 6.25.

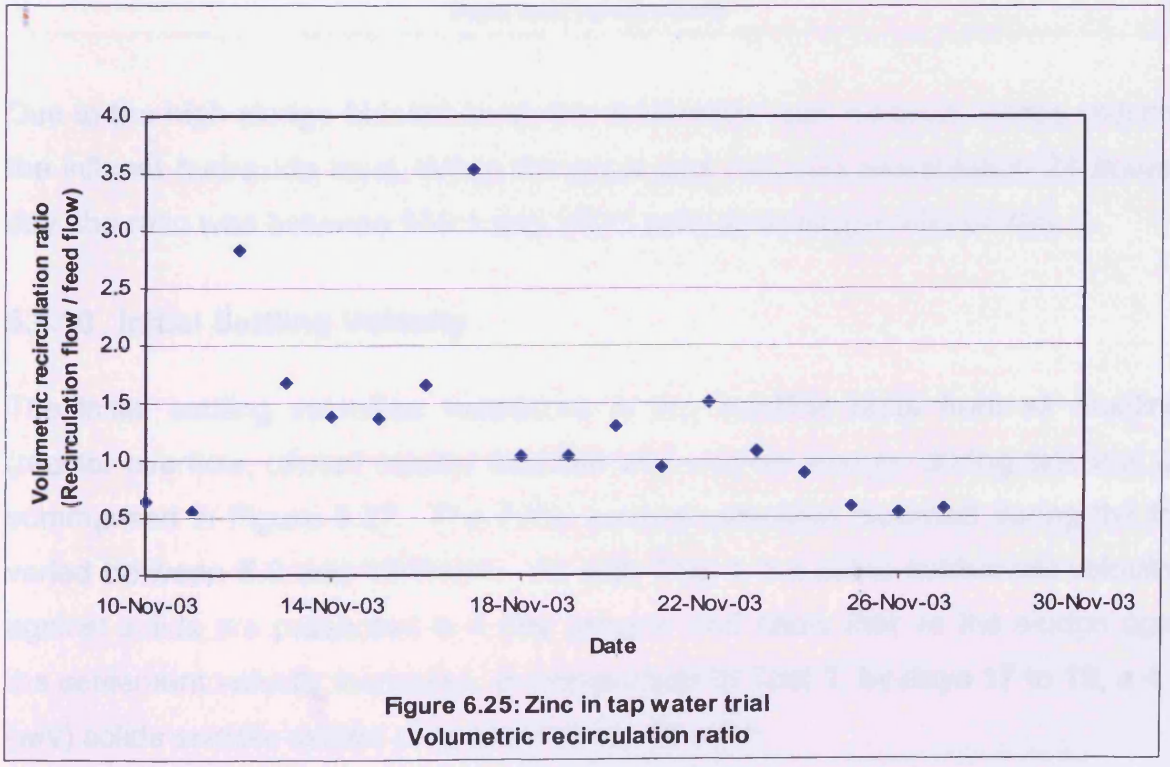


Figure 6.25: Zinc in tap water trial
Volumetric recirculation ratio

6.5.9 Mass Recirculation Ratio

Figure 6.26 shows the mass recirculation ratio during the zinc trial. The mass recirculation ratio varied between 5:1 and 690: 1 during the whole trial. The ratio of 690:1 occurred on the 17th November 2003, when sludge had built up in the clarifier during the previous 2 day period.

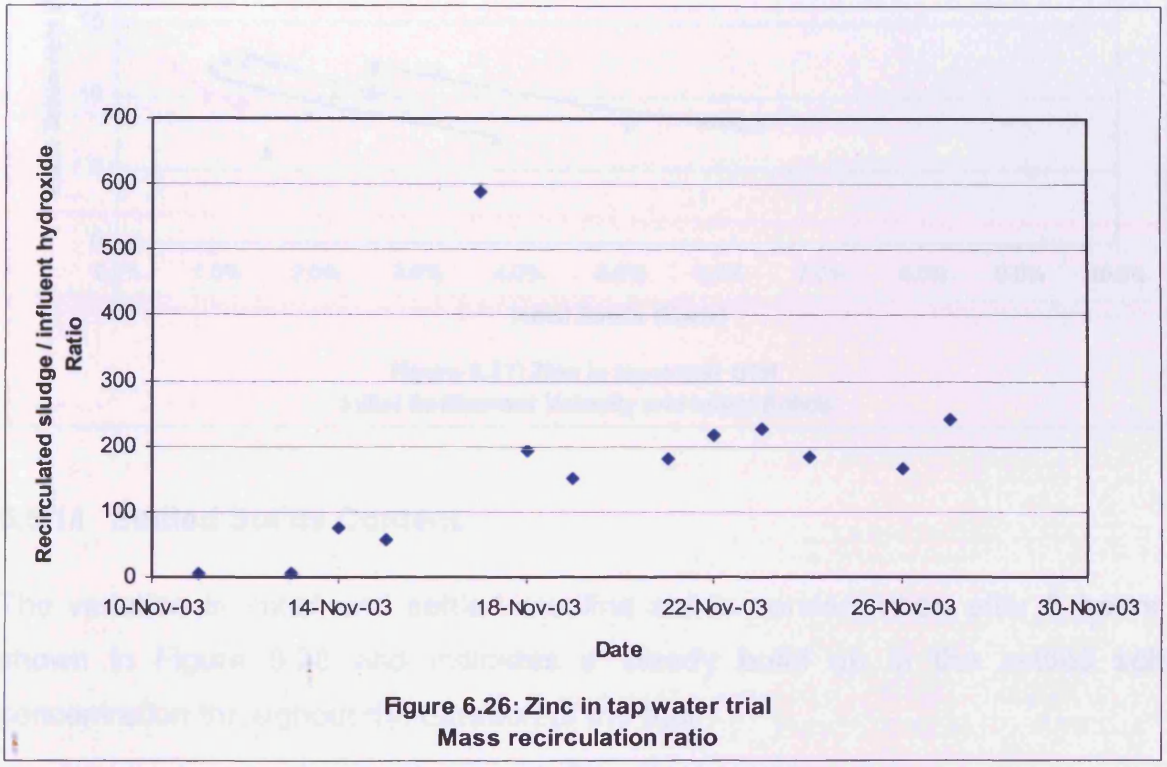


Figure 6.26: Zinc in tap water trial Mass recirculation ratio

Due to the high sludge blanket level, the feed water was reduced, hence reducing the influent hydroxide level. When the plant was run with recirculation 24 hours a day, the ratio was between 150:1 and 260:1 with an average ratio of 206: 1.

6.5.10 Initial Settling Velocity

The initial settling velocities measured in the mudline tests from all mudlines (reactor overflow, diluted reactor overflow and recycle sludge) during zinc trial are summarised in Figure 6.27. The initial settling velocities recorded during the trial varied between 6.0 and 12.7m/hr. As with Trial 1 the initial settlement velocities against solids are presented in 4 day groups, and show that as the sludge ages, the settlement velocity increases. In comparison to Trial 1, by days 17 to 19, a 4 % (w/v) solids sample settled at approximately 10 m/hr.

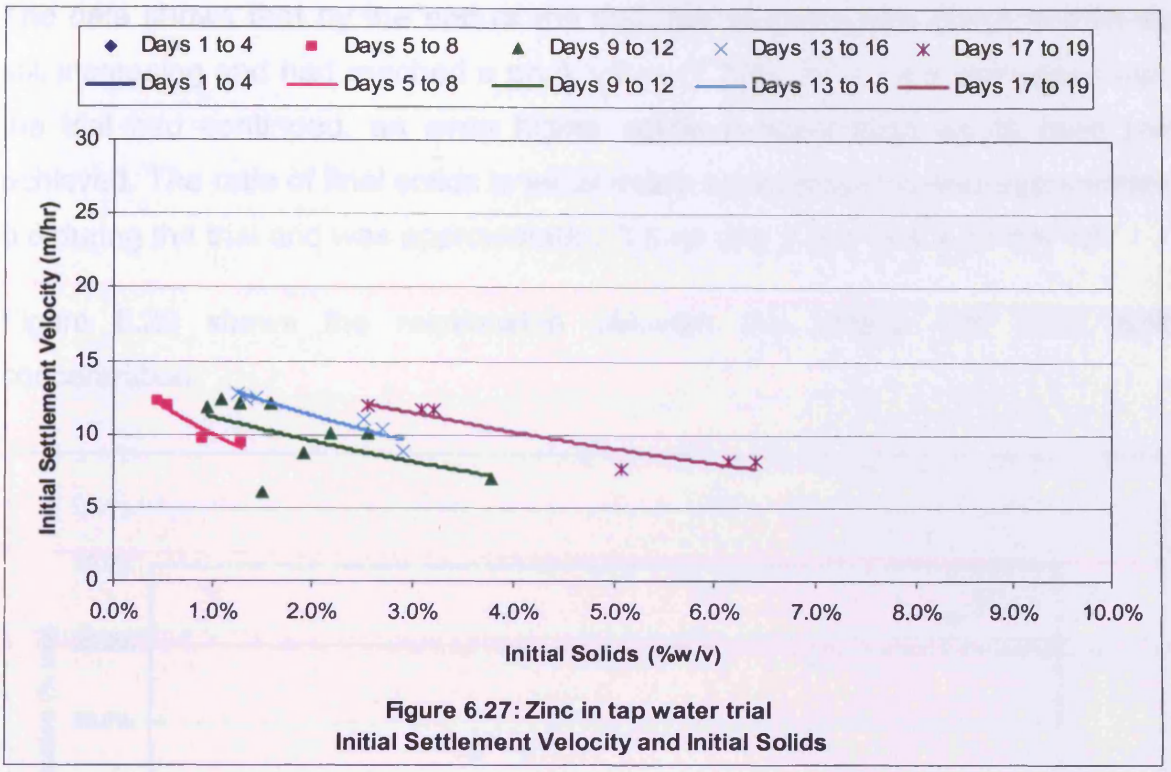


Figure 6.27: Zinc in tap water trial
Initial Settlement Velocity and Initial Solids

6.5.11 Settled Solids Content

The variation in initial and settled mudline solids concentration after 2 hours is shown in Figure 6.28 and indicates a steady build up in the settled solids concentration throughout the duration of the trial.

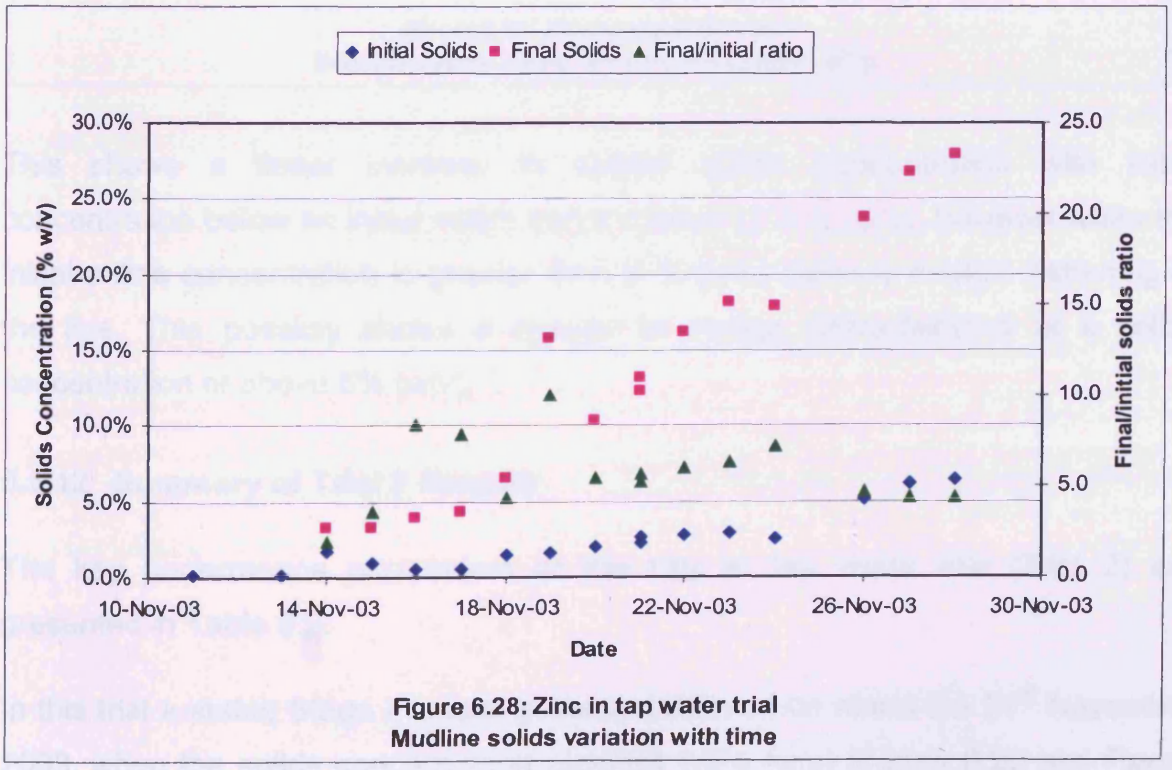


Figure 6.28: Zinc in tap water trial
Mudline solids variation with time

The data shows that by the end of the trial, the settled solids concentration was still increasing and had reached a peak value of 28% (w/v). It is envisaged that if the trial had continued, an even higher solids concentration would have been achieved. The ratio of final solids to initial solids concentrations was approximately 5.8 during the trial and was approximately 3.6 on day 5 and of 4.4 on day 18.

Figure 6.29 shows the relationship between the settled and initial solids concentration.

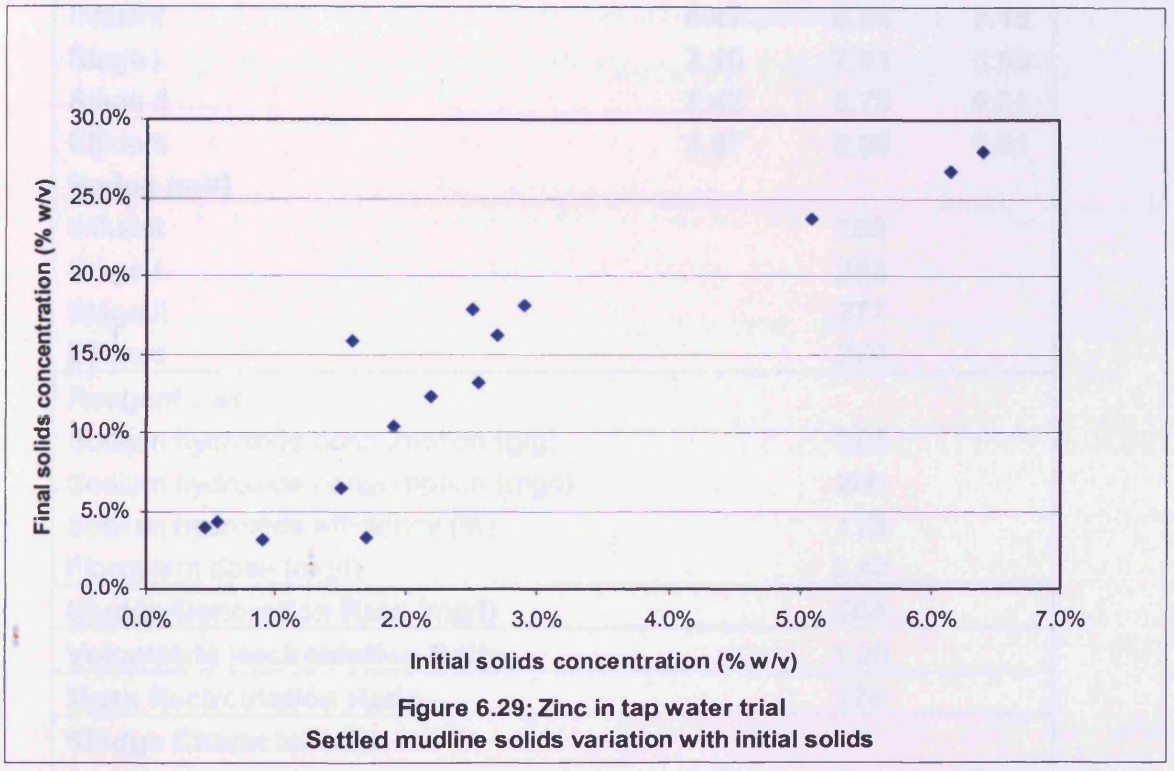


Figure 6.29: Zinc in tap water trial
Settled mudline solids variation with initial solids

This shows a linear increase in settled solids concentration with initial concentration below an initial solids concentration of 3 % (w/v), however when the initial solids concentration is greater than 5 % (w/v) there is a slight flattening of the line. This possibly shows a change in sludge characteristics at a solids concentration of above 5% (w/v).

6.5.12 Summary of Trial 2 Results

The key performance parameters of the zinc in tap water trial (Trial 2) are presented in Table 6.9.

In this trial a stable Stage I reactor pH was achieved on about the 21st November 2003, when the solids concentration reached 1.5% (w/v) (Figure 6.20 and Figure 6.21).

Table 6.9: Trial 2 key performance parameters

	Min	Average	Max
Flow rates			
Average feed flow rate (l/hr)		9.8	
Average recirculation flow rate (l/hr)		10.7	
Feed Metals (mg/l)			
Calculated average Zn		154	
Retention Time (min)			
Stage I/ Stage II	11.1	15.3	19.3
pH (pH units)			
Influent	6.47	6.84	7.15
Stage I	7.10	7.91	8.60
Stage II	8.43	8.78	9.61
Effluent	8.67	8.95	9.61
Redox (mV)			
Influent		268	
Stage I		288	
Stage II		277	
Effluent		270	
Reagent Use			
Sodium hydroxide consumption (g/g)		1.08	
Sodium hydroxide consumption (mg/l)		205	
Sodium hydroxide efficiency (%)		113	
Flocculant dose (mg/l)		3.43	
Sludge Generation Rate (mg/l)		268	
Volumetric Recirculation Ratio		1.28	
Mass Recirculation Ratio		176	
Sludge Characteristics			
Reactor Solids (g/l)	1.00	23.1	64.0
2 Hour Settled Solids (g/l)	32.1	136	279
Recycle solids (g/l)	1.00	56.4	136
Initial settling Velocity (m/hr)	6.02	104	12.7
Final/ Initial solids ratio	1.95	5.77	10.0

On the 26th November 2003, day 17 of the trial, the final/initial flocculation tank solids ratio was 4.7.

In comparison to Trial 1, by days 17 to 19, a 4 % (w/v) solids sample settled at approximately 10 m/hr.

6.6 Trial 3 – Aluminium in Tap Water

6.6.1 Trial 3 Introduction

The aluminium water trial was run between the 1st December 2003 and 19th December 2003. Key stages during this trial were:

- 1st December 2003, plant set up and commissioning;
- 1st December 2003 to 9th December 2003, build up of sludge mass and development of High Density Sludge (HDS) operating conditions;
- 9th December 2003 to 19th December 2003, operation of the plant in HDS mode.

Aluminium nitrate powder was added directly to an IBC full of pH 3 tap water. On the 11th December 2003, the aluminium nitrate was replaced with aluminium sulphate, which was added as a liquid concentrate. As with all the trials, the desired feed flow rate was 10l/hour. The calculated feed flow rate was 7.4 l/hr, with an average aluminium concentration of 143mg/l. The operating pH of the Stage II reactor during the trial was 6.5.

6.6.2 Plant Water Quality

Water quality samples were taken of the influent and effluent water on the 12th December 2003, and showed the influent and effluent total aluminium concentrations were 232.6 mg/l and 0.66 mg/l respectively.

6.6.3 Plant Flows and Reactor Retention Time

The plant feed and recirculation flow rates are presented in Figure 6.30. The average feed rate during the trial was 7.4 l/hr, whilst the recirculation flow rate averaged 13.17 l/hr. The reactor retention time during the aluminium trial, presented in Figure 6.30, varied between 8 and 30 minutes, with an average of 17 minutes.

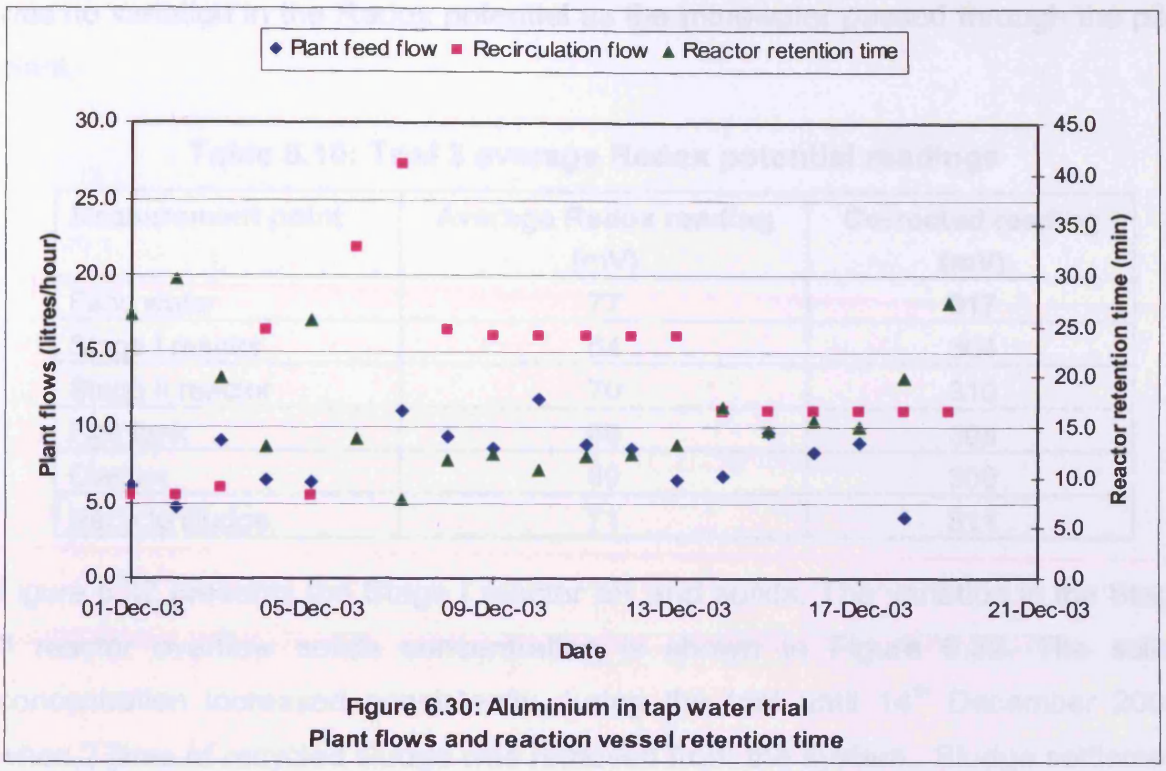


Figure 6.30: Aluminium in tap water trial
Plant flows and reaction vessel retention time

6.6.4 System pH, Redox Potential and Reactor Solids Concentration

The variation of pH throughout the aluminium trial is presented in Figure 6.31.

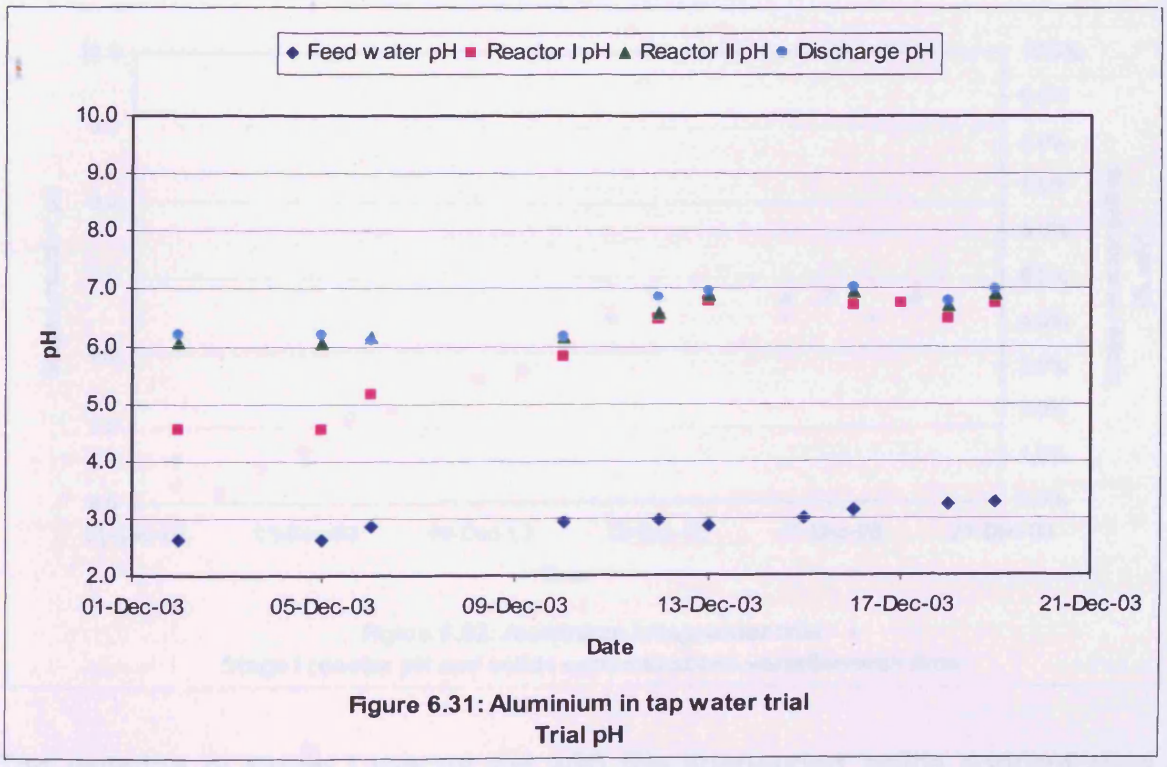


Figure 6.31: Aluminium in tap water trial
Trial pH

The average stage Redox potential measurements and the corrected values are presented in Table 6.10. As with Trail 2, the readings would indicate that there

was no variation in the Redox potential as the minewater passed through the pilot plant.

Table 6.10: Trial 3 average Redox potential readings

Measurement point	Average Redox reading (mV)	Corrected reading (mV)
Feed water	77	317
Stage I reactor	64	304
Stage II reactor	70	310
Floc tank	68	308
Clarifier	69	309
Recycle sludge	71	311

Figure 6.32 presents the Stage I reactor pH and solids. The variation in the Stage II reactor overflow solids concentration is shown in Figure 6.32. The solids concentration increased consistently during the trial until 14th December 2003, when 2 litres of recycled sludge was removed from the system. Sludge settlement tests were undertaken on the removed sludge. The solids concentration was maintained between 4% and 5% (w/v) after the 14th December 2003.

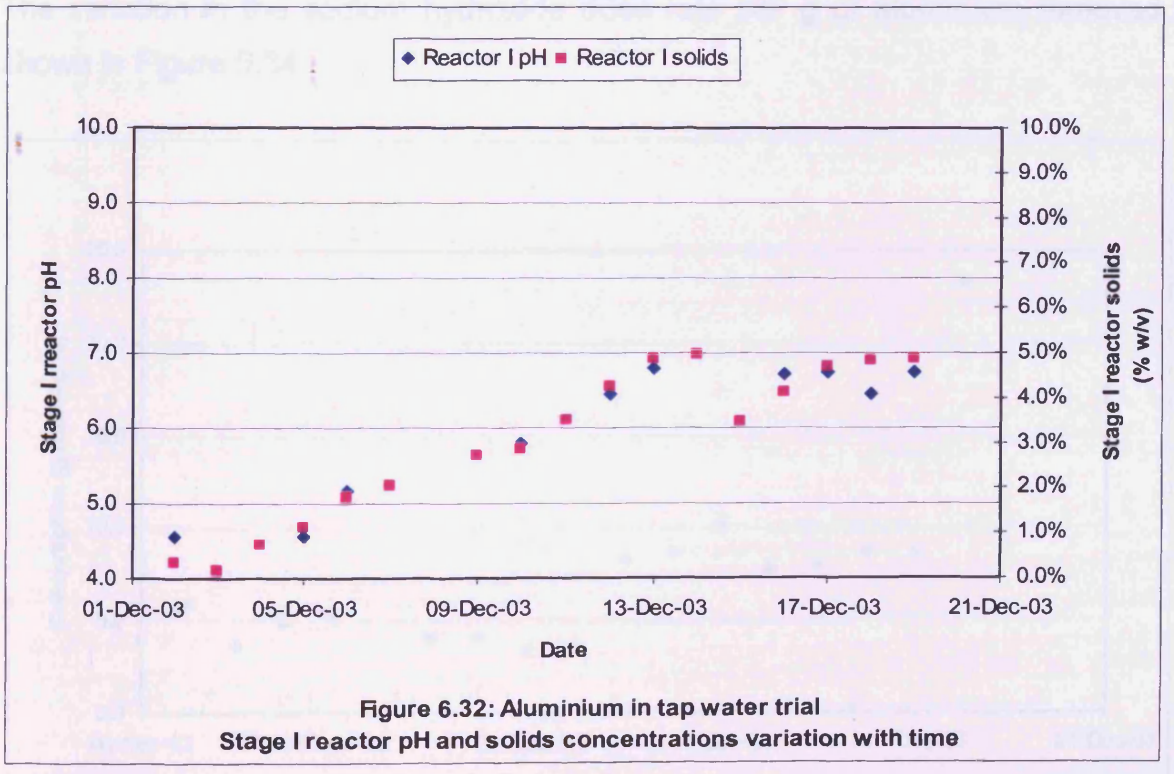


Figure 6.32: Aluminium in tap water trial
Stage I reactor pH and solids concentrations variation with time

The variation of Stage I reactor pH with the suspended solids concentration is shown in Figure 6.33 and indicates that the Stage I reactor pH stabilised when the reactor solids concentration exceeded 4% (w/v).

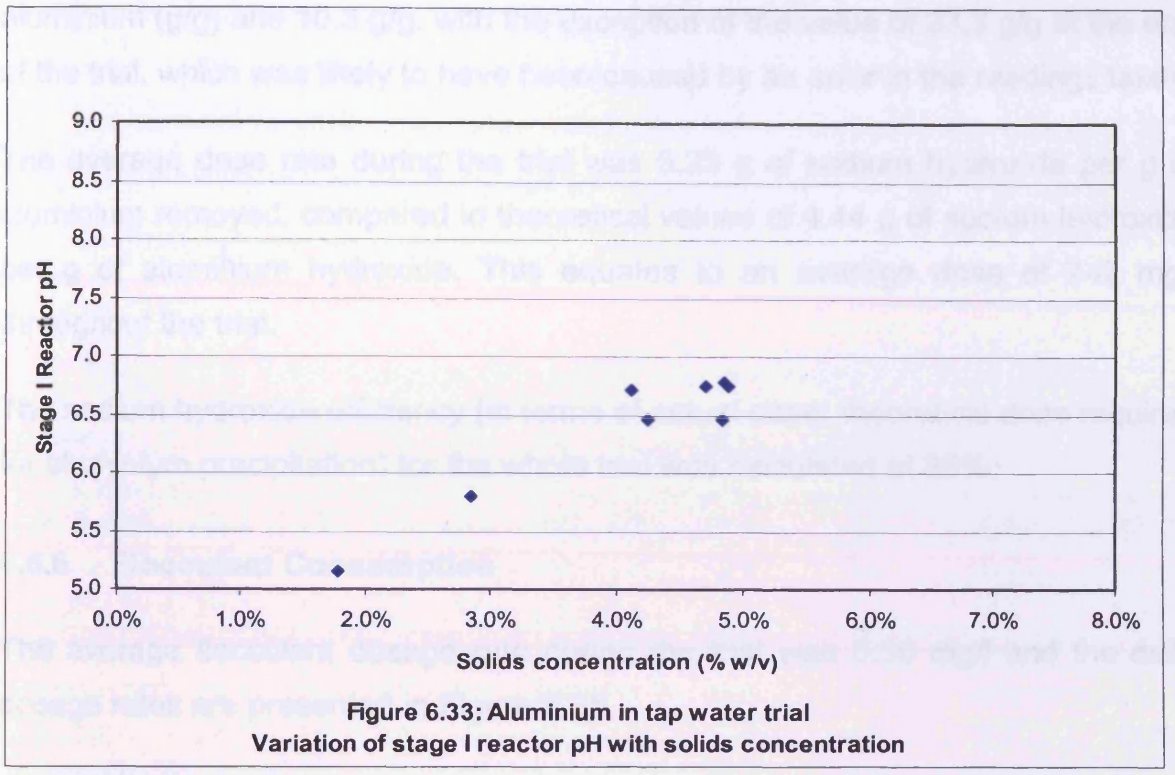


Figure 6.33: Aluminium in tap water trial
Variation of stage I reactor pH with solids concentration

6.6.5 Sodium Hydroxide Consumption

The variation in the sodium hydroxide dose rate per g of aluminium removed is shown in Figure 6.34.

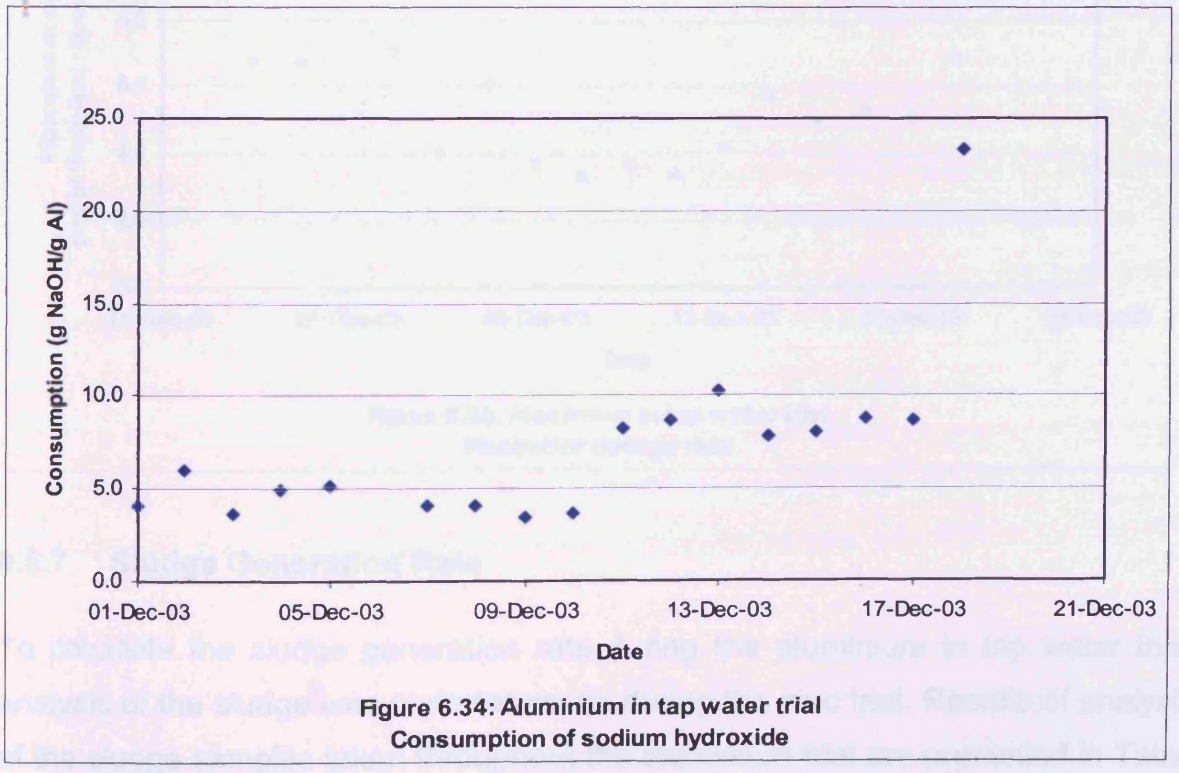


Figure 6.34: Aluminium in tap water trial
Consumption of sodium hydroxide

This reveals that the dose rate varied between 3.4 g of sodium hydroxide per g of

aluminium (g/g) and 10.3 g/g, with the exception of the value of 23.3 g/g at the end of the trial, which was likely to have been caused by an error in the readings taken.

The average dose rate during the trial was 5.23 g of sodium hydroxide per g of aluminium removed, compared to theoretical values of 4.44 g of sodium hydroxide per g of aluminium hydroxide. This equates to an average dose of 747 mg/l throughout the trial.

The sodium hydroxide efficiency (in terms of actual dose/ theoretical dose required for aluminium precipitation) for the whole trial was calculated at 85%.

6.6.6 Flocculant Consumption

The average flocculant dosage rate during the trial was 5.56 mg/l and the daily dosage rates are presented in Figure 6.35.

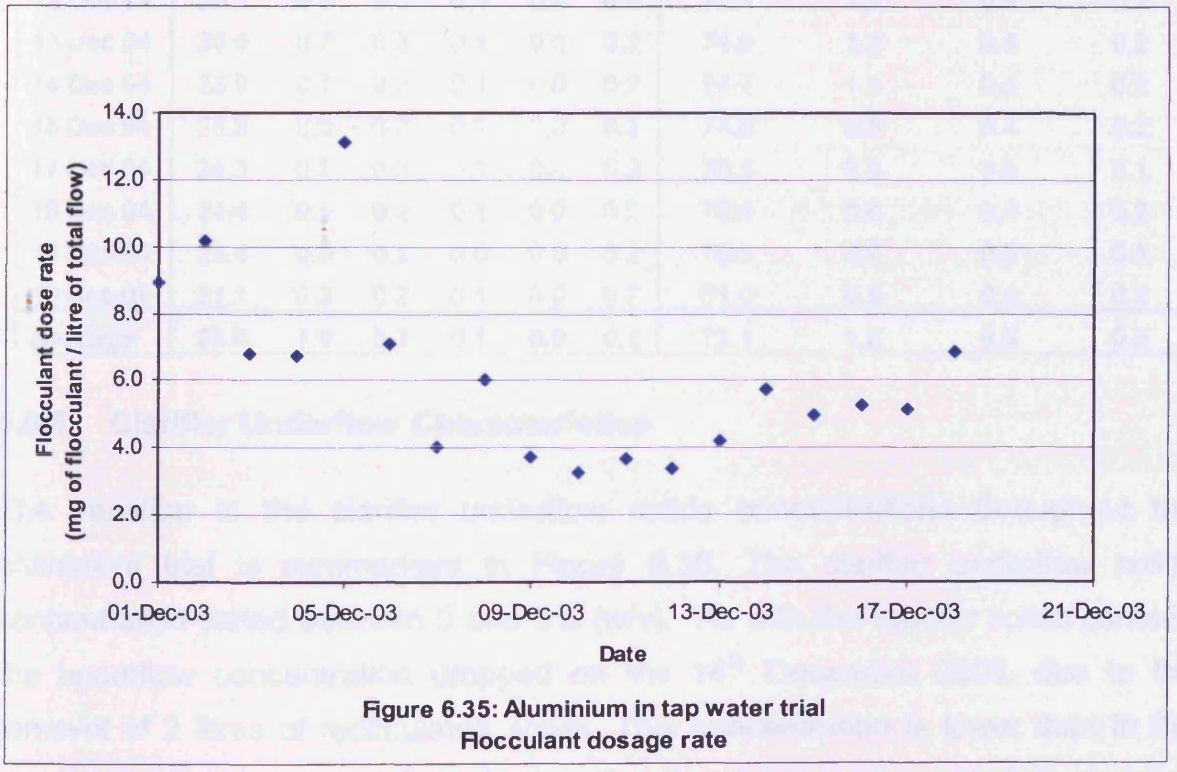


Figure 6.35: Aluminium in tap water trial
Flocculant dosage rate

6.6.7 Sludge Generation Rate

To calculate the sludge generation rate during the aluminium in tap water trial, analysis of the sludge was undertaken, as during the zinc trial. Results of analysis of the sludge samples taken throughout the aluminium trial are presented in Table 6.11.

The results indicate that the dry solids produced during the pilot plant trials contained 25.0% aluminium compared to a theoretical value of 34.6%. Assuming that the aluminium was in the form of aluminium hydroxide, this resulted in a sludge generation rate of 4g of sludge per g of aluminium removed or by using an influent aluminium concentration of 150 mg/l, and a solids generation rate of 600 mg/l.

Table 6.11: Trial 3 sludge dry solids composition (%of total solids)

Date	Al	Zn	Fe	Ca	Co	Si	$AlOH_3$	$Zn(OH)_2$	$Fe(OH)_3$	$CaCO_3$
	%	%	%	%	%	%	%	%	%	%
04 Dec 04	25.7	2.0	0.4	0.1	0.0	0.2	74.3	3.0	0.8	0.1
05 Dec 04	27.1	2.0	0.4	0.1	0.0	0.2	78.4	3.0	0.7	0.1
06 Dec 04	25.8	1.8	0.4	0.0	0.0	0.2	74.6	2.7	0.8	0.0
07 Dec 04	24.8	1.4	0.3	0.1	0.0	0.2	71.7	2.2	0.5	0.1
10 Dec 04	22.6	0.9	0.2	0.1	0.0	0.2	65.2	1.4	0.4	0.1
11 Dec 04	24.5	1.1	0.3	0.1	0.0	0.2	70.8	1.6	0.5	0.1
12 Dec 04	25.1	0.8	0.3	0.1	0.0	0.2	72.4	1.2	0.5	0.2
13 Dec 04	25.9	0.7	0.3	0.1	0.0	0.2	74.9	1.1	0.6	0.2
14 Dec 04	25.9	0.7	0.2	0.1	0.0	0.2	74.7	1.1	0.5	0.2
15 Dec 04	25.8	0.5	0.2	0.1	0.0	0.2	74.6	0.8	0.4	0.2
17 Dec 04	24.3	0.5	0.3	0.1	0.0	0.2	70.3	0.8	0.5	0.1
18 Dec 04	24.4	0.5	0.2	0.1	0.0	0.2	70.4	0.8	0.4	0.2
18 Dec 04	26.4	0.5	0.2	0.0	0.0	0.2	76.3	0.7	0.5	0.1
19 Dec 04	21.1	0.3	0.2	0.1	0.0	0.2	61.0	0.5	0.4	0.2
Average	**25.0**	**1.0**	**0.3**	**0.1**	**0.0**	**0.2**	**72.1**	**1.5**	**0.5**	**0.2**

6.6.8 Clarifier Underflow Characteristics

The variation in the clarifier underflow solids concentrations throughout the aluminium trial is summarised in Figure 6.36. The clarifier underflow solids concentration varied between 0 and 5% (w/v). As with the reactor solids content, the underflow concentration dropped on the 14th December 2003, due to the removal of 2 litres of recirculated solids. This concentration is lower than in the previous trials and resulted from the fact that the sludge settlement characteristics (see Section 6.6.11) were not as high as the previous trials.

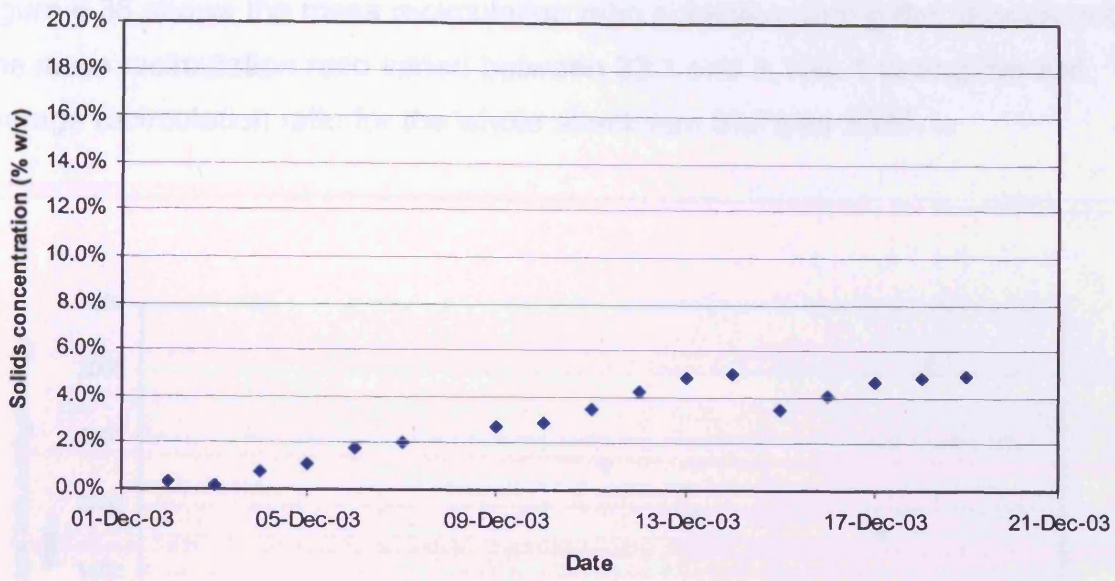


Figure 6.36: Aluminium in tap water trial
Variation in clarifier underflow solids concentration

6.6.9 Volumetric Recirculation Ratio

The variation of the volumetric recirculation ratio throughout the aluminium trial is shown in Figure 6.37. Due to the need to maintain a higher recirculation flow rate, the volumetric recirculation ratio was higher than in the previous trials and averaged 1.7 during the trial.

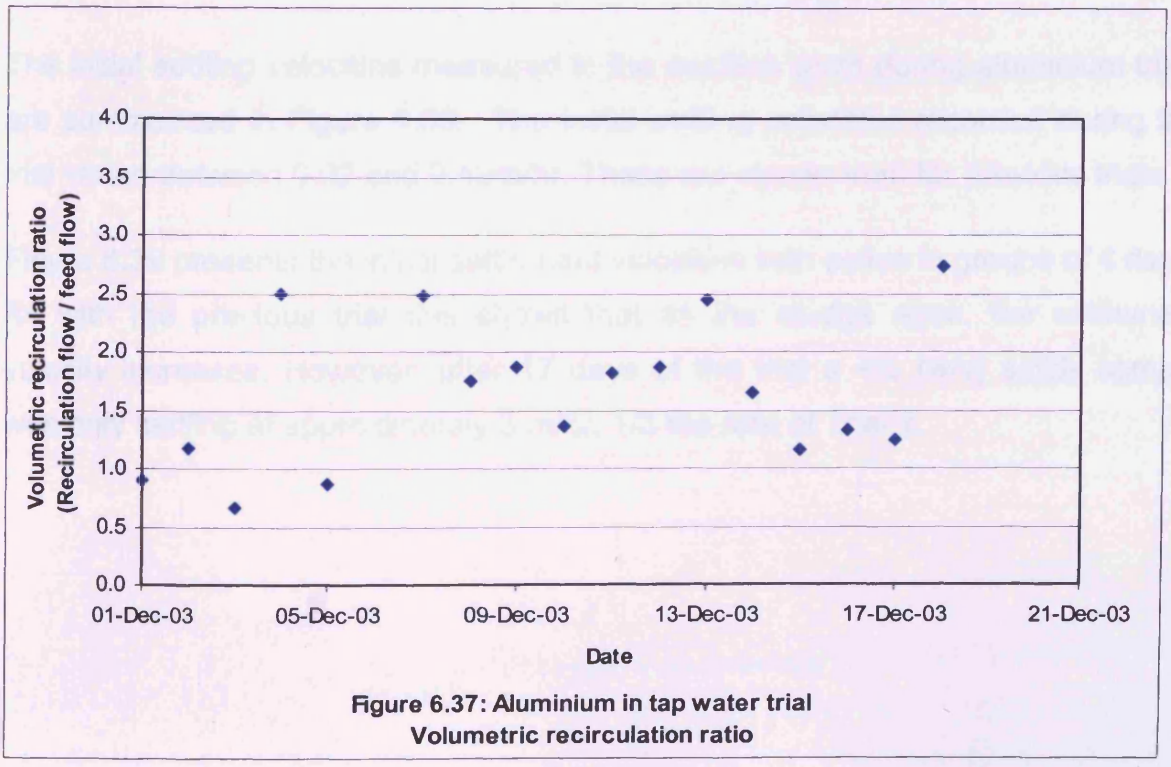


Figure 6.37: Aluminium in tap water trial
Volumetric recirculation ratio

6.6.10 Mass Recirculation Ratio

Figure 6.38 shows the mass recirculation ratio achieved during the aluminium trial. The mass recirculation ratio varied between 22:1 and 3,108: 1 during the trial. The average recirculation ratio for the whole aluminium trial was 1035:1.

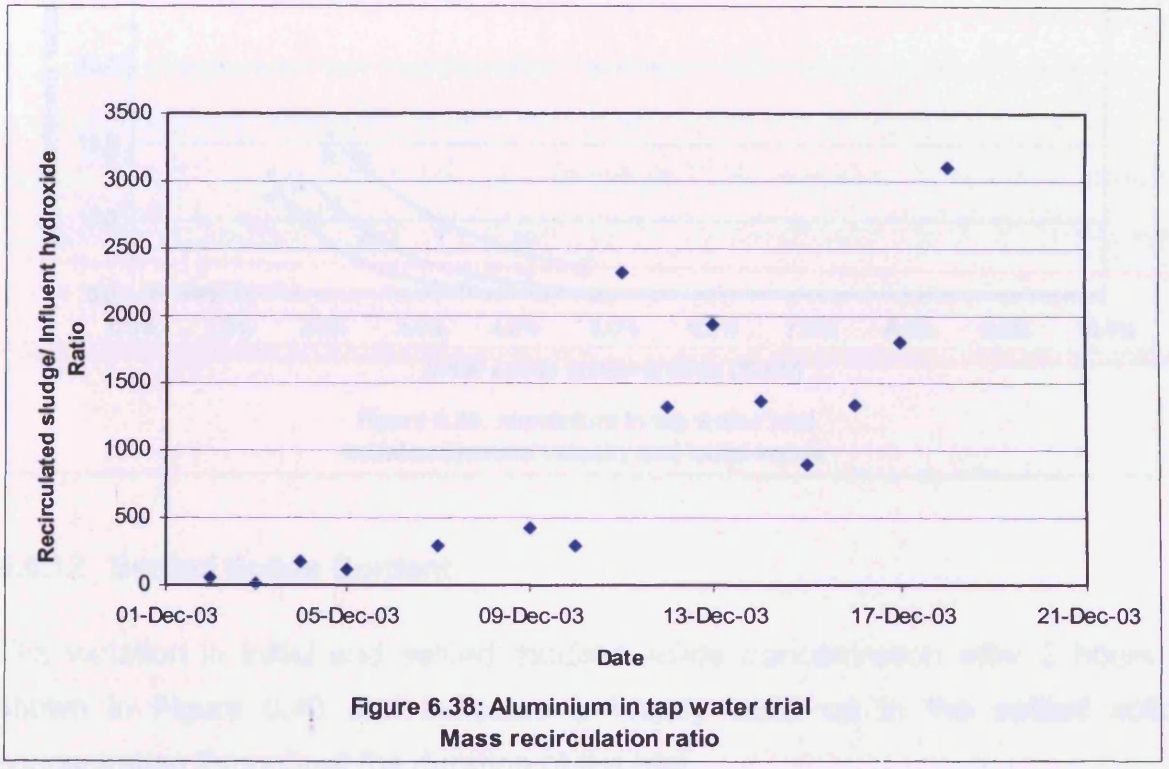


Figure 6.38: Aluminium in tap water trial Mass recirculation ratio

6.6.11 Initial Settling Velocity

The initial settling velocities measured in the mudline tests during aluminium trials are summarised in Figure 6.39. The initial settling velocities recorded during the trial varied between 0.02 and 9.49m/hr. These are slower than for previous trials.

Figure 6.39 presents the initial settlement velocities with solids in groups of 4 days. As with the previous trial this shows that as the sludge ages, the settlement velocity increases. However, after 17 days of the trial a 4% (w/v) solids sample was only settling at approximately 3 m/hr, 1/3 the rate of Trial 2.

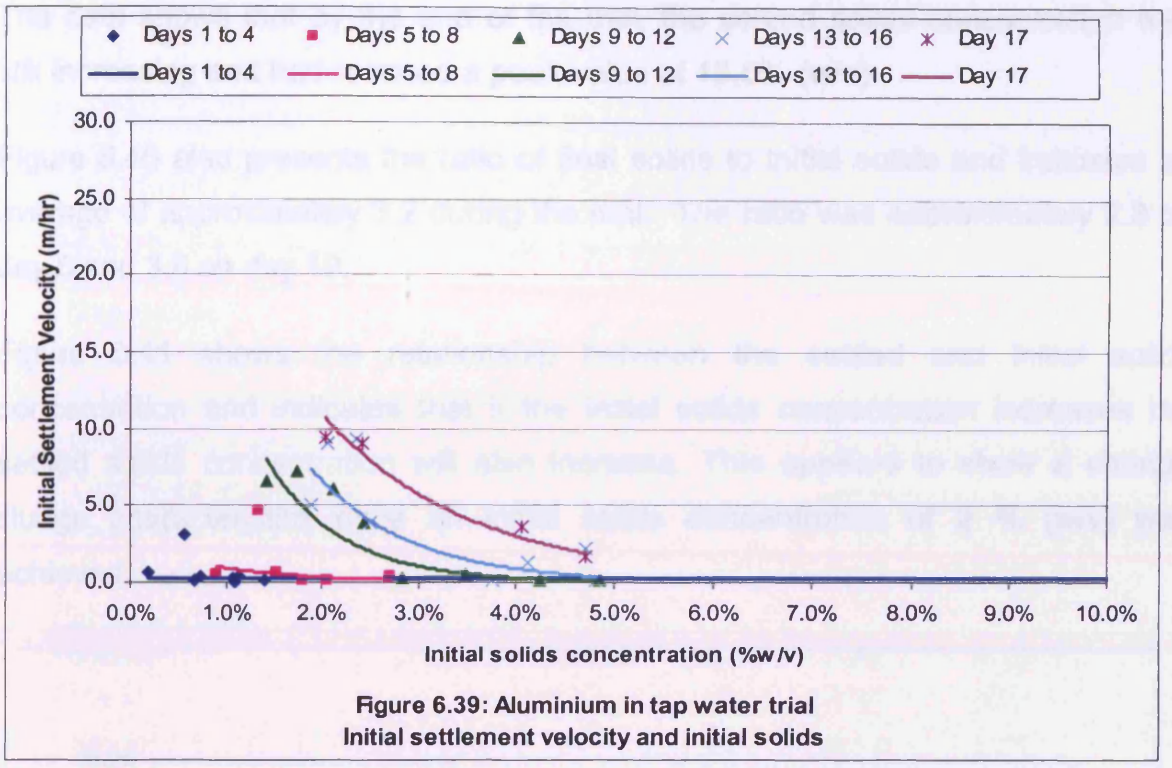


Figure 6.39: Aluminium in tap water trial
Initial settlement velocity and initial solids

6.6.12 Settled Solids Content

The variation in initial and settled mudline solids concentration after 2 hours is shown in Figure 6.40 and indicates a steady build up in the settled solids concentration throughout the duration of the trial.

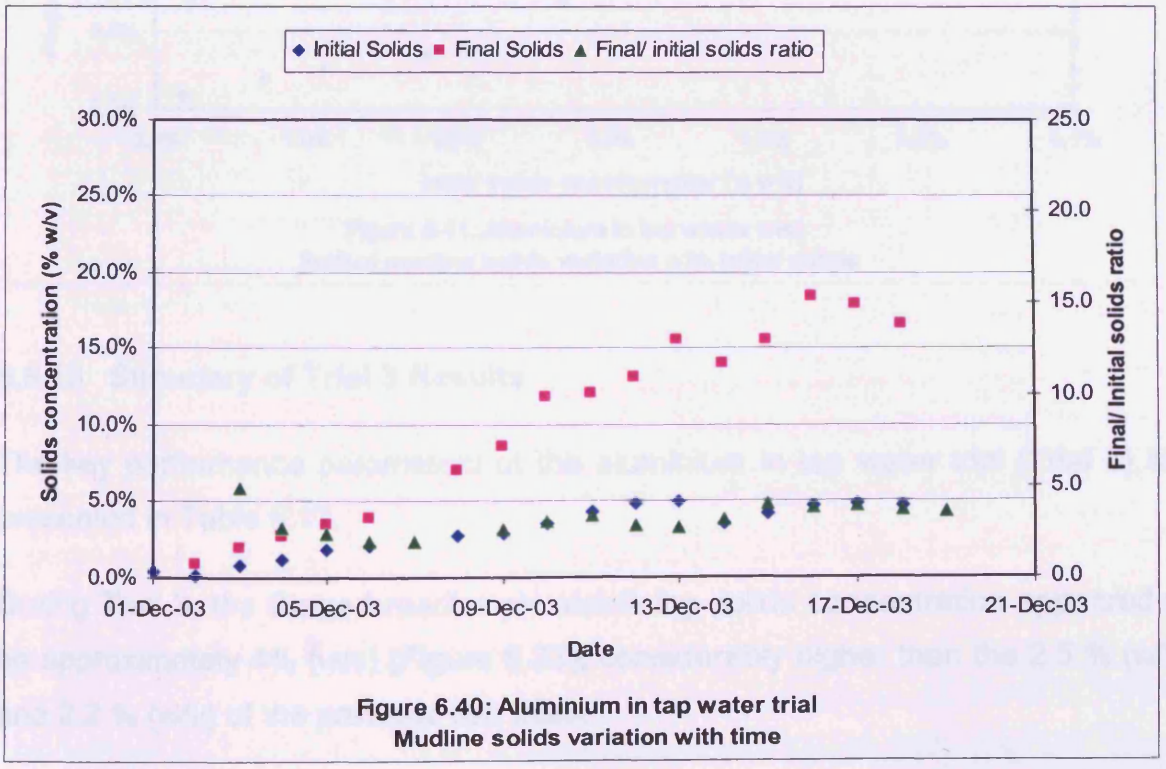


Figure 6.40: Aluminium in tap water trial
Mudline solids variation with time

The data shows that by the end of the trial, the settled solids concentration was still increasing and had reached a peak value of 18.5% (w/v).

Figure 6.40 also presents the ratio of final solids to initial solids and indicates an average of approximately 3.2 during the trial. The ratio was approximately 2.3 on day 5 and 3.6 on day 19.

Figure 6.41 shows the relationship between the settled and initial solids concentration and indicates that if the initial solids concentration increases the settled solids concentration will also increase. This appears to show a change sludge characteristics once an initial solids concentration of 2 % (w/v) was achieved.

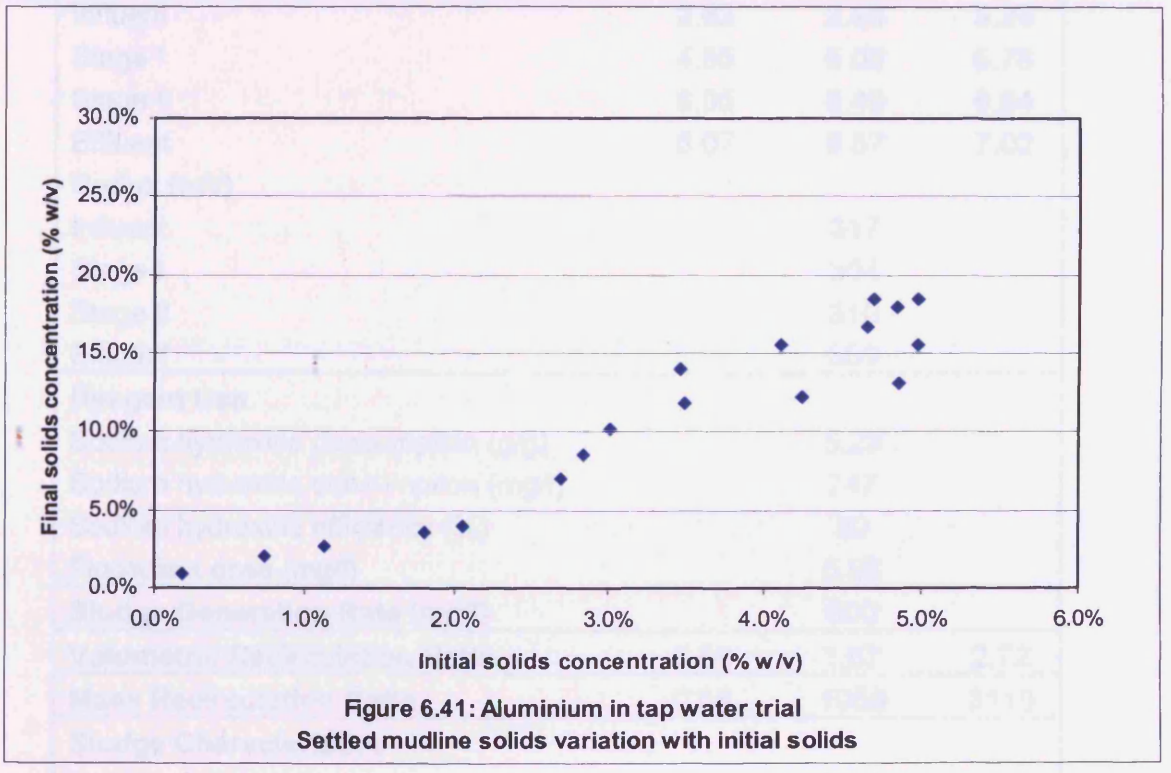


Figure 6.41: Aluminium in tap water trial
Settled mudline solids variation with initial solids

6.6.13 Summary of Trial 3 Results

The key performance parameters of the aluminium in tap water trial (Trial 3) are presented in Table 6.12.

During Trial 3, the Stage I reactor pH stabilising solids concentration appeared to be approximately 4% (w/v) (Figure 6.33), considerably higher than the 2.5 % (w/v) and 2.2 % (w/v) of the previous two trials.

On the 19th December 2003, day 19 of the trial, the final/initial flocculation tank

solids ratio was 3.6. In comparison to two previous trials, by day 17 a 4 % (w/v) solids sample settled at approximately 3 m/hr, approximately 1/3 the rate of the previous trials.

Table 6.12: Trial 3 key performance parameters

	Min	Average	Max
Flow rates			
Average feed flow rate (l/hr)		7,4	
Average recirculation flow rate (l/hr)		13.2	
Feed Metals (mg/l)			
Calculated average Al		143	
Retention Time (min)			
Stage I/ Stage II	7.83	16.7	29.6
pH (pH units)			
Influent	2.63	2.95	3.28
Stage I	4.55	6.00	6.78
Stage II	6.05	6.49	6.94
Effluent	6.07	6.57	7.02
Redox (mV)			
Influent		317	
Stage I		304	
Stage II		310	
Effluent		309	
Reagent Use			
Sodium hydroxide consumption (g/g)		5.23	
Sodium hydroxide consumption (mg/l)		747	
Sodium hydroxide efficiency (%)		89	
Flocculant dose (mg/l)		5.56	
Sludge Generation Rate (mg/l)		600	
Volumetric Recirculation Ratio	0.66	1.67	2.72
Mass Recirculation Ratio	0.66	1060	3110
Sludge Characteristics			
Reactor Solids (g/l)	1.90	30.1	49.7
2 Hour Settled Solids (g/l)	9.30	102	185
Recycle solids (g/l)	2.90	30.2	49.7
Initial settling Velocity (m/hr)	0.02	2.83	9.49
Final/ Initial solids ratio	1.92	3.16	4.89

6.7 Trial 4 – Manganese in Tap Water

6.7.1 Trial 4 Introduction

The manganese water trial was run between the 11th March 2004 and 30th March 2004. Key stages during this trial were:

- 11th March 2004, plant set up and commissioning;
- 11th March 2004 to 20th March 2004, build up of sludge mass and development of High Density Sludge (HDS) operating conditions;
- 20th March 2004 to 30th March 2004, operation of the plant in run with HDS operating conditions.

Manganese was added in the form of manganese chloride to an IBC full of pH 3 tap water. On the 13th and 29th March 2004, part of the manganese was added as manganese sulphate. As with all the trials, the desired feed flow rate was 10l/hour. The calculated feed flow rate was 9.6 l/hr with an average manganese concentration of 188mg/l.

The operating pH of the Stage II reactor during the trial was 9.25.

6.7.2 Plant Water Quality

Water quality samples were taken of the influent and effluent water during the trial. These are presented in Table 6.13 and indicate that as the sludge aged the treatment improved. Due to limited water quality analysis in previous trials, this was not previously detected. The effluent manganese concentrations on the 25th and 26th March 2004 were caused by a decrease in the discharge pH. It is unclear why this occurred, though it could have been due to the general increase in the Stage I reactor pH. No Stage I reactor manganese concentrations are available to confirm this.

Table 6.13: Trial 4 water quality analysis results – Total manganese

Date	Total Influent (mg/l)	Total Effluent (mg/l)	Filtered Effluent (mg/l)
15 Mar 04 12:20	144	7.09	6.24
15 Mar 04 11:00	6.86	6.40	7.22
16 Mar 04	345	4.90	5.20
18 Mar 04	159	-	5.57
19 Mar 04	190	1.70	1.70
19 Mar 04	185	1.50	1.60
25 Mar 04	187	2.70	2.48
26 Mar 04	178	2.86	2.53
30 Mar 04	237	0.49	0.54

6.7.3 Plant Flows and Reactor Retention Time

The plant feed and recirculation flow rates are presented in Figure 6.42. The average feed rate during the trial was 9.6 l/hr whilst the recirculation flow rate averaged 11.3 l/hr.

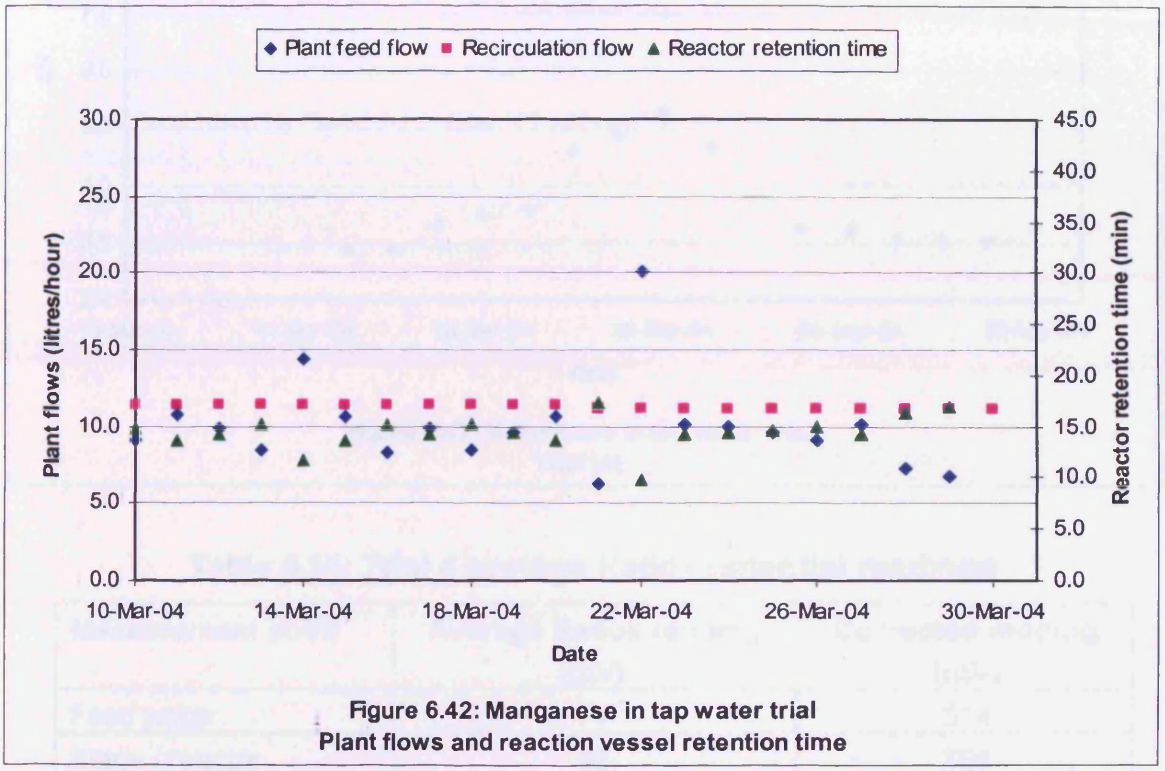


Figure 6.42: Manganese in tap water trial
Plant flows and reaction vessel retention time

The reactor retention time during the manganese trial, presented in Figure 6.42, varied between 9.1 and 16.8 minutes, with an average of 13.8 minutes.

6.7.4 System pH, Redox Potential and Reactor Solids Concentration

The pH variation throughout the aluminium trial is presented in Figure 6.43. A blockage occurred in the recycle line during the night of the 24th March 2004, resulting in a loss of solids from the system; this resulted in the pH in the Stage I reactor dropping slightly.

The average Redox potential measurements are presented in Table 6.14. As with Trail 1, the readings would indicate that as the minewater passed through the pilot plant the fluids become less oxidizing, as shown by the decrease in the Redox potential readings in the feed water and the clarifier contents.

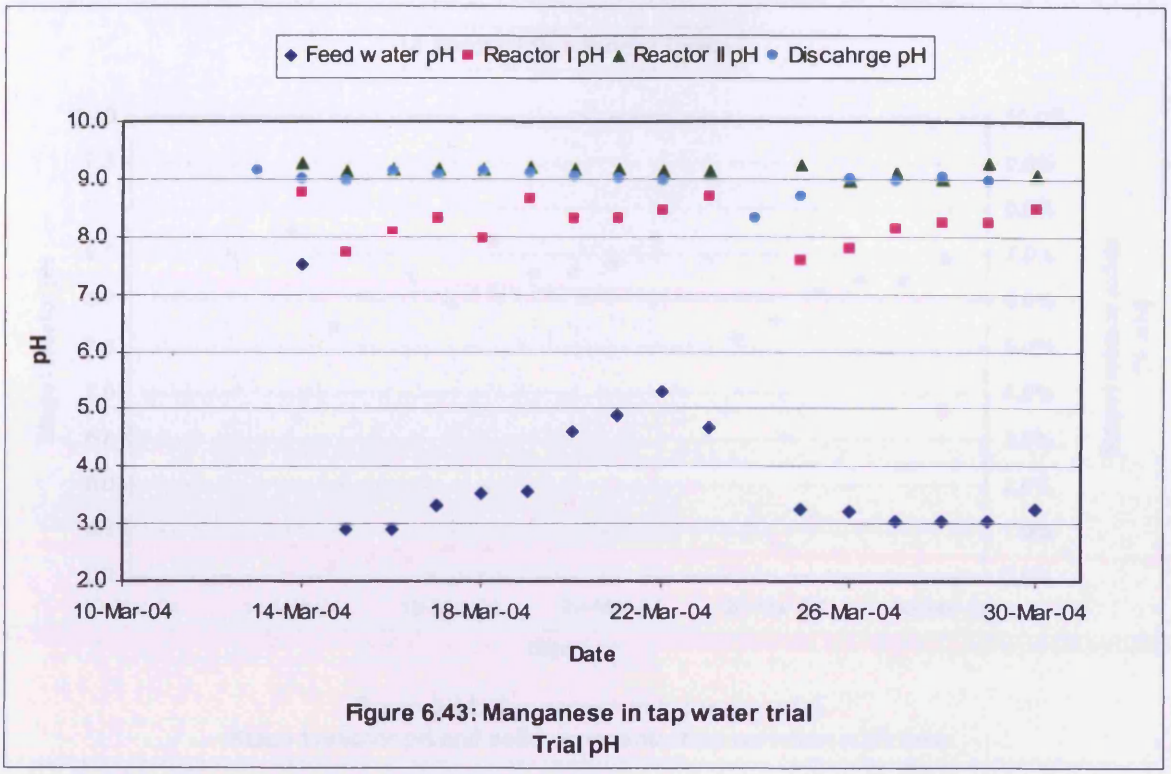


Figure 6.43: Manganese in tap water trial
Trial pH

Table 6.14: Trial 4 average Redox potential readings

Measurement point	Average Redox reading (mV)	Corrected reading (mV)
Feed water	74	314
Stage I reactor	18	258
Stage II reactor	7	247
Floc tank	0	240
Clarifier	-8	232
Recycle sludge	-37	203

Figure 6.44 presents the Stage I reactor pH and solids, and shows that both were adversely affected by a blockage in the recirculation line on the 24th March 2004. The blockage in the recycle line resulted in a loss of solids from the system. However, the sludge appeared to immediately stabilise after the loss of solids and no sludge acclimatisation was required.

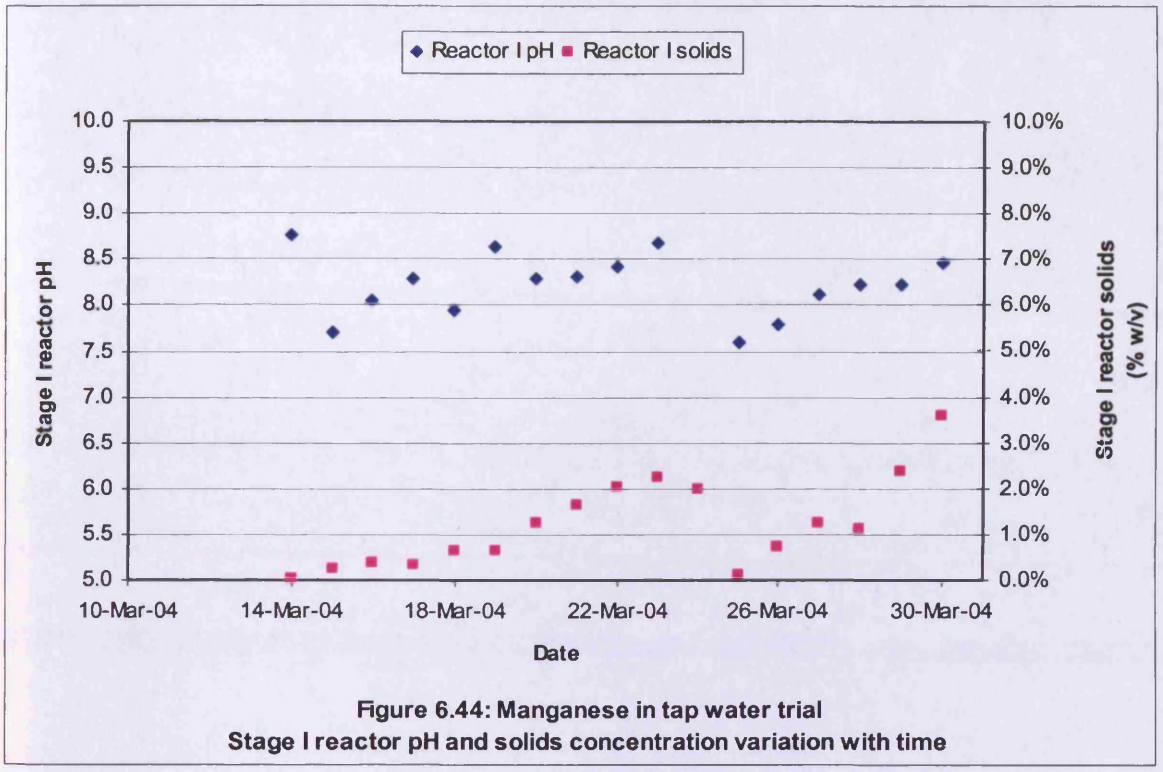


Figure 6.44: Manganese in tap water trial
Stage I reactor pH and solids concentration variation with time

The variation of Stage I reactor pH with the solids concentration is shown in Figure 6.45, stabilising at a reactor solids concentration of above 1.5% (w/v).

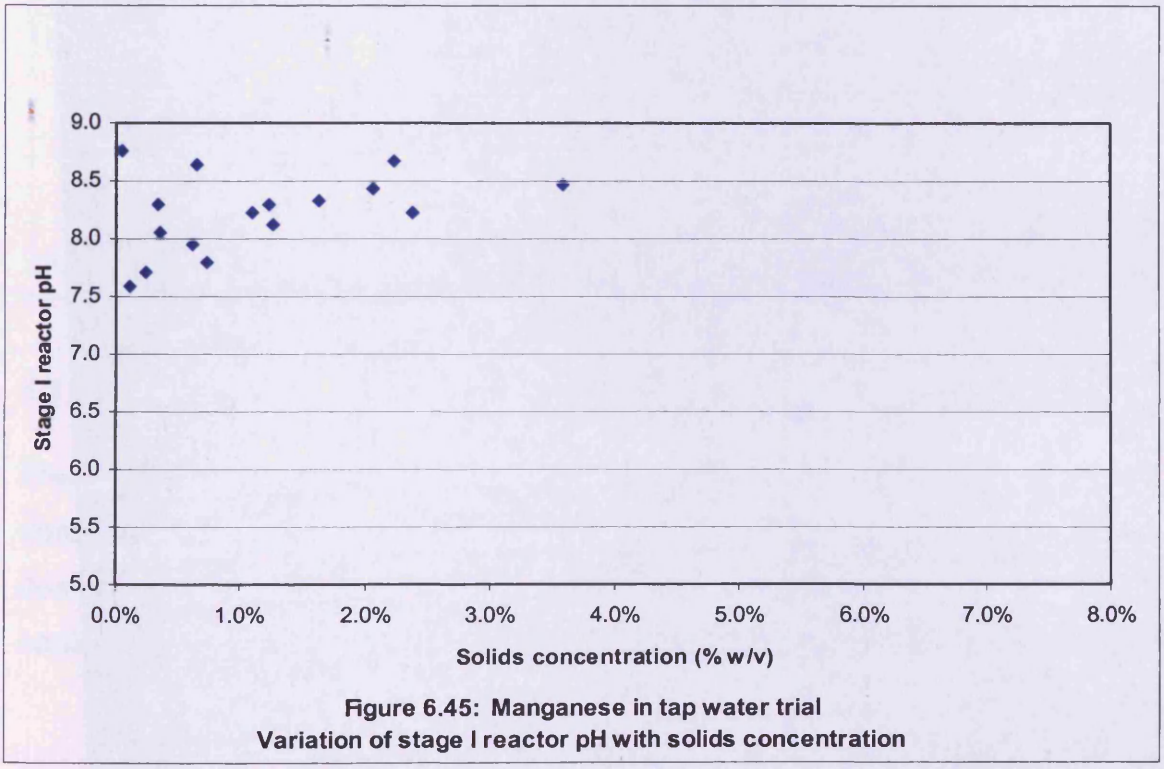


Figure 6.45: Manganese in tap water trial
Variation of stage I reactor pH with solids concentration

6.7.5 Sodium Hydroxide Consumption

The variation in the sodium hydroxide dose rate per gram of manganese removed

is shown in Figure 6.46. This reveals that the dose rate varied between 0.79g/g and 2.93g/g. The average dose rate during the trial was 1.81g of sodium hydroxide per g of manganese removed, compared to theoretical values of 1.41g of sodium hydroxide per g of manganese, assuming that the manganese is removed as manganese oxy-hydroxide (MnOOH). This equates to an average dose of 339 mg/l.

The sodium hydroxide efficiency (in terms of actual dose/ theoretical dose required for manganese precipitation) for the whole trial was calculated at 78%.

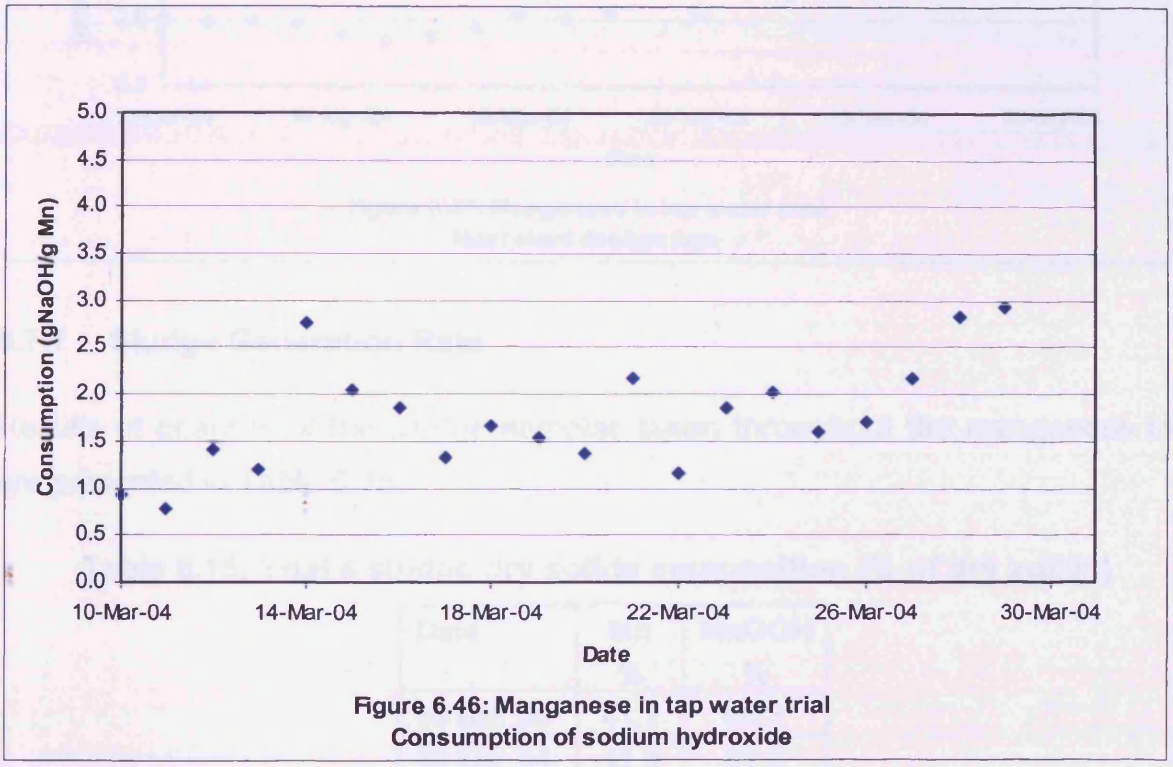


Figure 6.46: Manganese in tap water trial
Consumption of sodium hydroxide

6.7.6 Flocculant Consumption

The average flocculant dosage rate during the trial was 2.27mg/l, and the daily dosage rates are presented in Figure 6.47. A steady increase in the flocculant dose was required during the trial, corresponding to an increase in the solids content in the system.

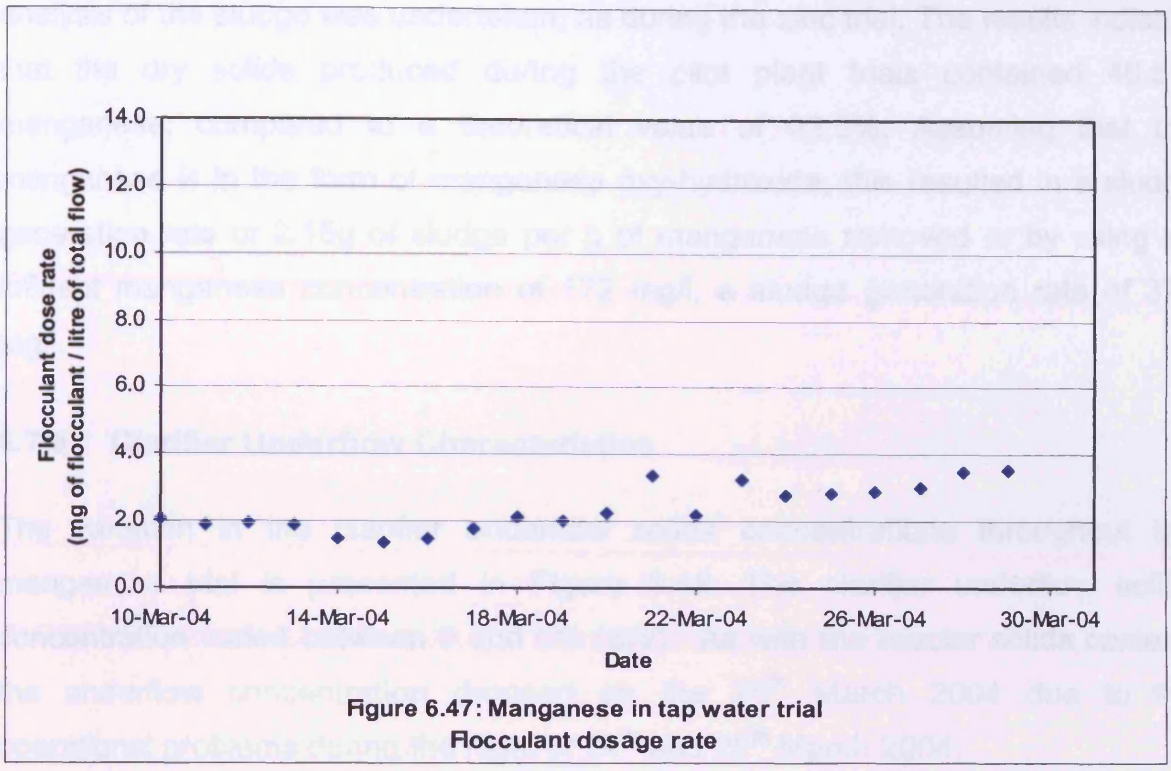


Figure 6.47: Manganese in tap water trial
Flocculant dosage rate

6.7.7 Sludge Generation Rate

Results of analysis of the sludge samples taken throughout the manganese trial are presented in Table 6.15.

Table 6.15: Trial 4 sludge dry solids composition (% of dry solids)

Date	Mn %	MnOOH %
15 Mar 04	41.7	66.7
16 Mar 04	41.8	67.0
18 Mar 04	45.4	72.6
19 Mar 04	42.7	68.3
21 Mar 04	46.9	75.0
22 Mar 04	45.4	72.6
23 Mar 04	47.5	76.0
24 Mar 04	45.6	72.9
25 Mar 04	47.9	76.7
26 Mar 04	48.4	77.4
27 Mar 04	48.8	78.1
28 Mar 04	49.6	79.3
29 Mar 04	50.8	81.2
30 Mar 04	48.9	78.2
Average	**46.5**	**74.4**

To calculate the sludge generation rate during the manganese in tap water trial,

analysis of the sludge was undertaken, as during the zinc trial. The results indicate that the dry solids produced during the pilot plant trials contained 46.5% manganese, compared to a theoretical value of 62.5%. Assuming that the manganese is in the form of manganese oxy-hydroxide, this resulted in a sludge generation rate of 2.15g of sludge per g of manganese removed or by using an influent manganese concentration of 172 mg/l, a sludge generation rate of 370 mg/l.

6.7.8 Clarifier Underflow Characteristics

The variation in the clarifier underflow solids concentrations throughout the manganese trial is presented in Figure 6.48. The clarifier underflow solids concentration varied between 0 and 5% (w/v). As with the reactor solids content, the underflow concentration dropped on the 25th March 2004 due to the operational problems during the night of 24th and 25th March 2004.

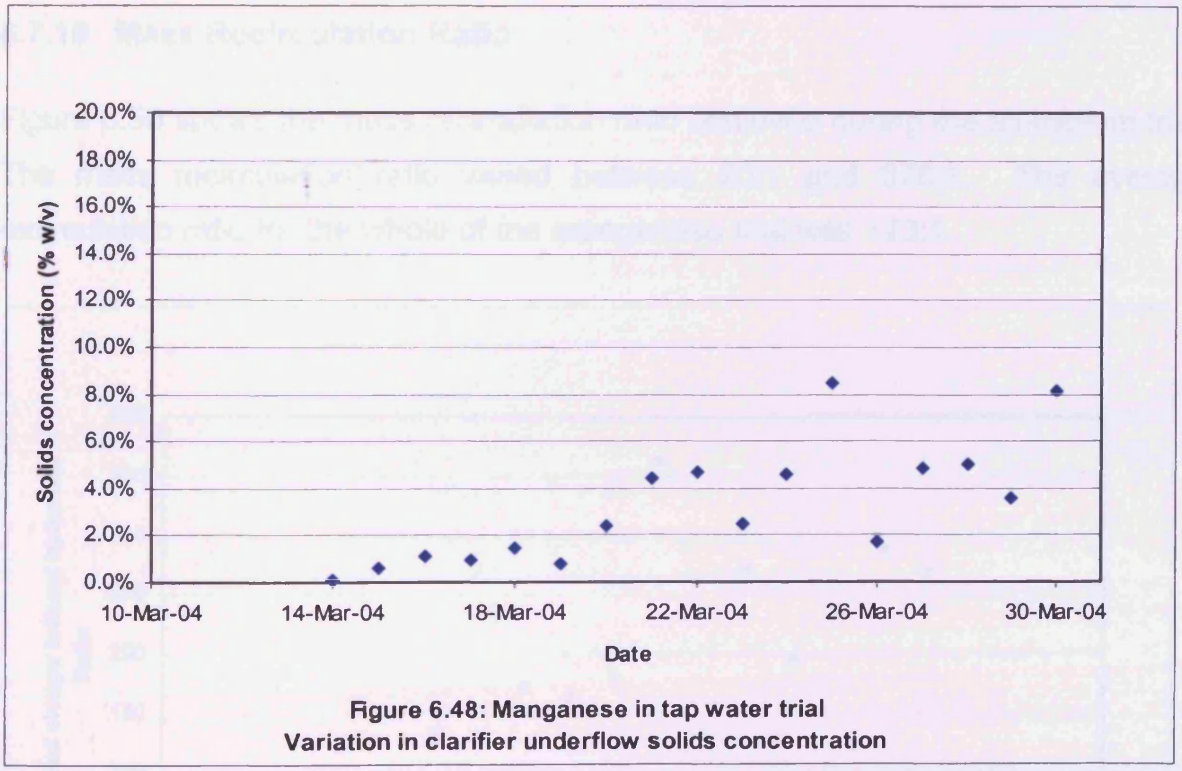


Figure 6.48: Manganese in tap water trial
Variation in clarifier underflow solids concentration

6.7.9 Volumetric Recirculation Ratio

The variation of the volumetric recirculation ratio throughout the manganese trial is shown in Figure 6.49 and averaged 1.2.

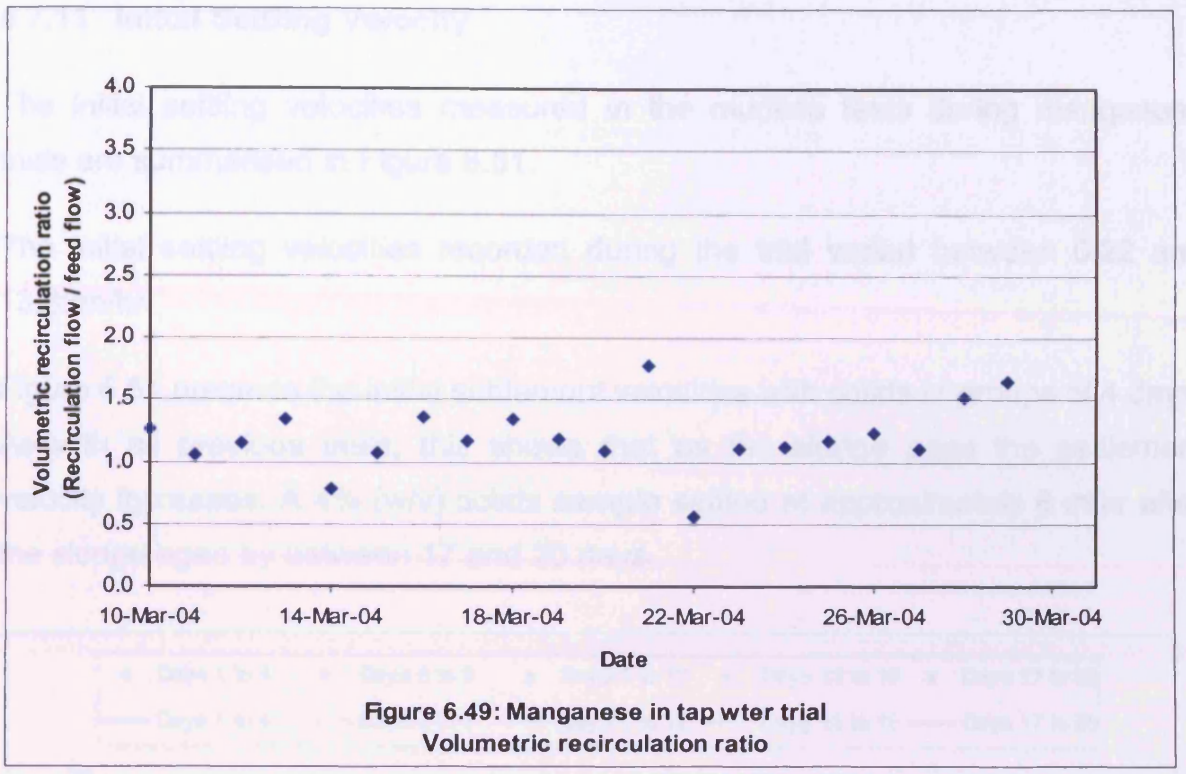


Figure 6.49: Manganese in tap wter trial
Volumetric recirculation ratio

6.7.10 Mass Recirculation Ratio

Figure 6.50 shows the mass recirculation ratio achieved during the aluminium trial. The mass recirculation ratio varied between 20:1 and 376:1. The average recirculation ratio for the whole of the manganese trial was 173:1.

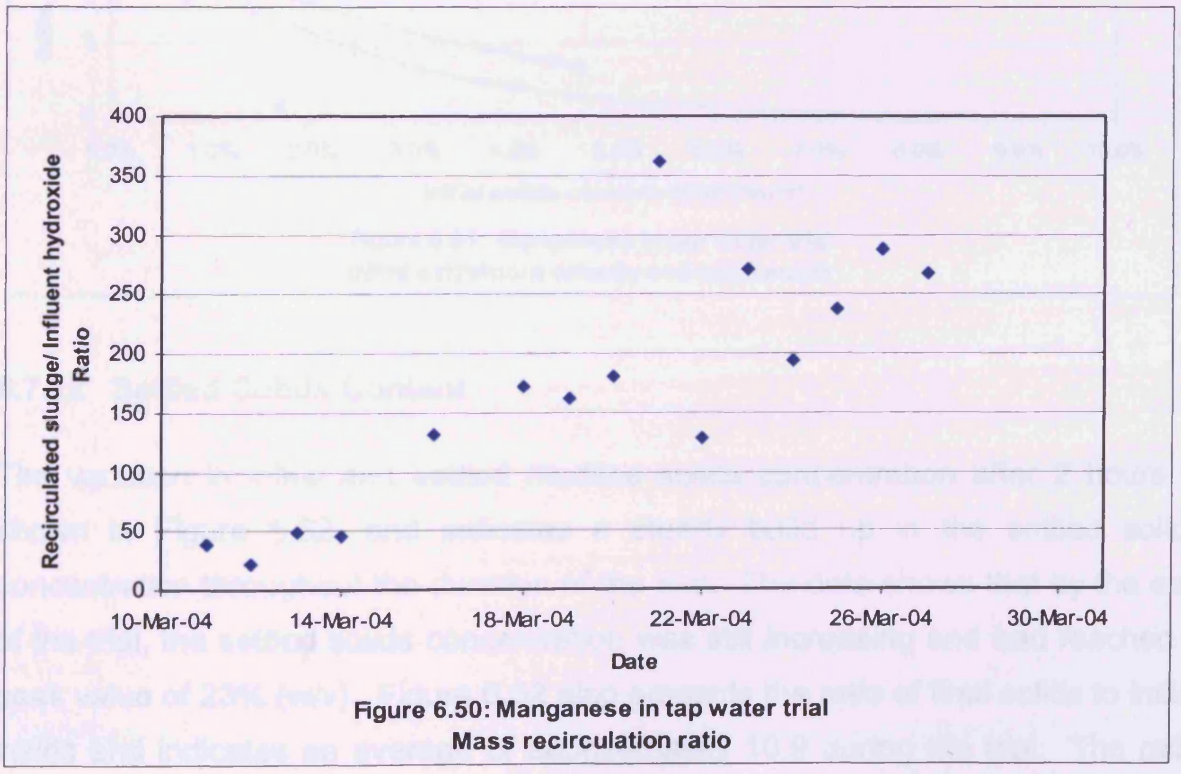


Figure 6.50: Manganese in tap water trial
Mass recirculation ratio

6.7.11 Initial Settling Velocity

The initial settling velocities measured in the mudline tests during manganese trials are summarised in Figure 6.51.

The initial settling velocities recorded during the trial varied between 0.22 and 13.39m/hr.

Figure 6.51 presents the initial settlement velocities with solids in groups of 4 days. As with all previous trials, this shows that as the sludge ages the settlement velocity increases. A 4% (w/v) solids sample settled at approximately 8 m/hr after the sludge aged by between 17 and 20 days.

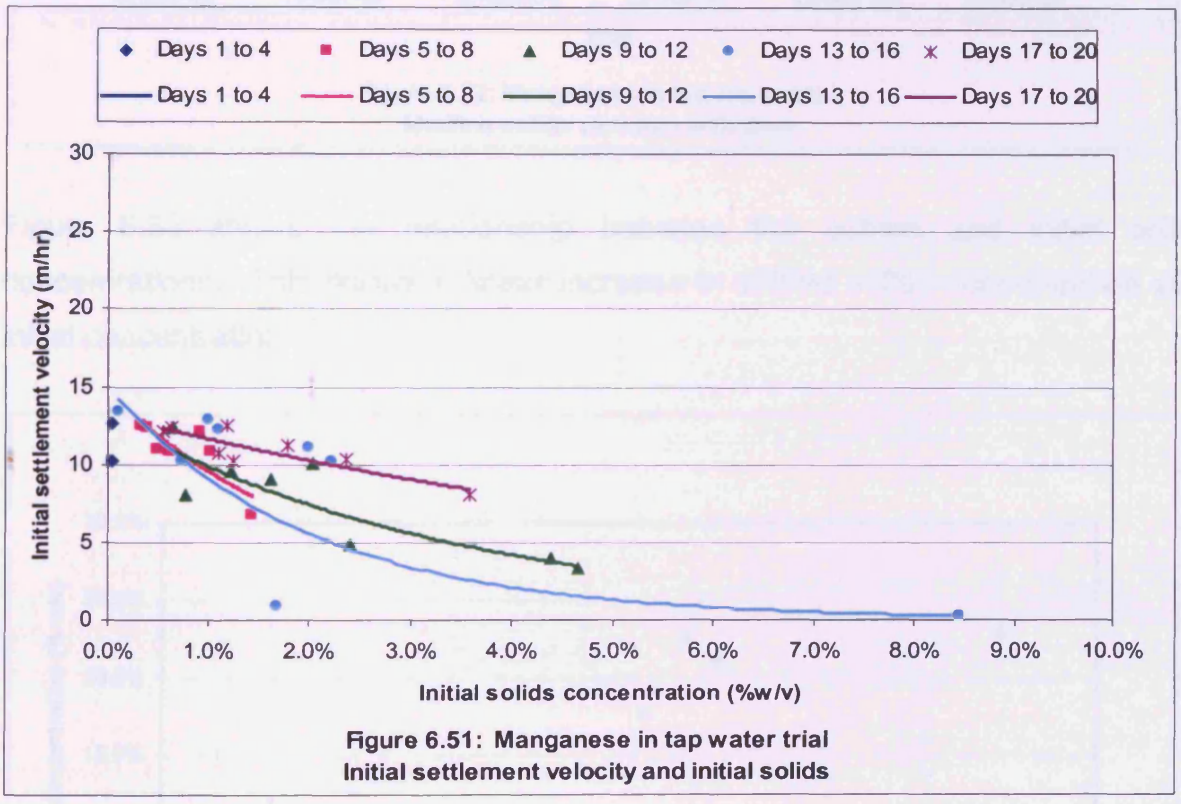


Figure 6.51: Manganese in tap water trial
Initial settlement velocity and initial solids

6.7.12 Settled Solids Content

The variation in initial and settled mudline solids concentration after 2 hours is shown in Figure 6.52, and indicates a steady build up in the settled solids concentration throughout the duration of the trial. The data shows that by the end of the trial, the settled solids concentration was still increasing and had reached a peak value of 23% (w/v). Figure 6.52 also presents the ratio of final solids to initial solids and indicates an average of approximately 10.9 during the trial. The ratio was approximately 16.8 on day 5 and 9.6 on day 19.

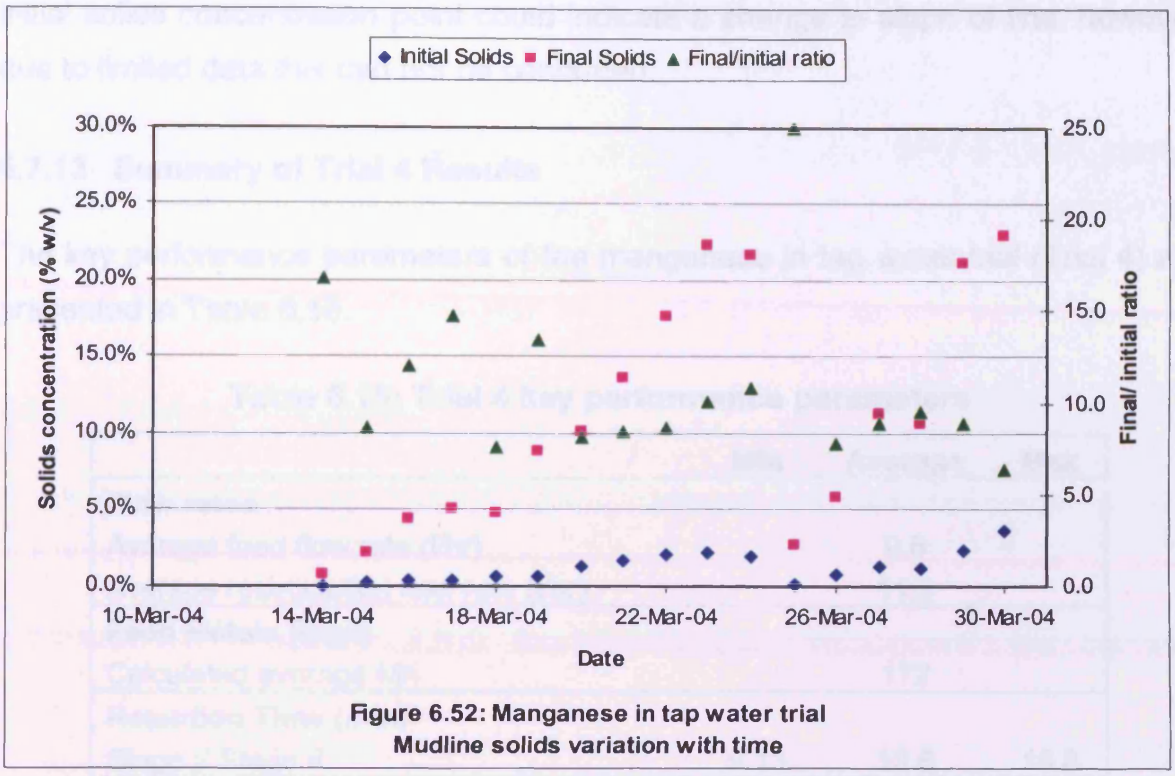


Figure 6.52: Manganese in tap water trial
Mudline solids variation with time

Figure 6.53 shows the relationship between the settled and initial solids concentrations. This shows a linear increase in settled solids concentration with initial concentration.

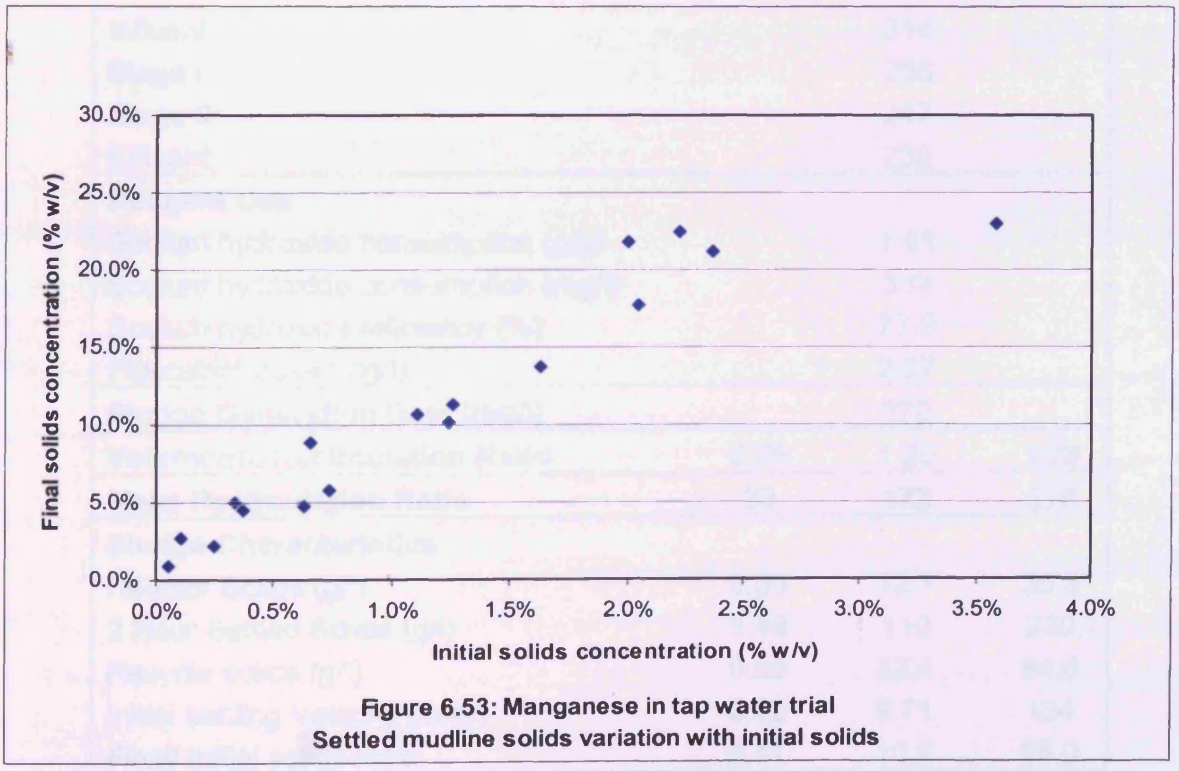


Figure 6.53: Manganese in tap water trial
Settled mudline solids variation with initial solids

The slope of a linear trend line through the data points in Figure 6.53 below an initial solids concentration of 2.5% (w/v) was approximately 8.9. The 3.5% (w/v)

initial solids concentration point could indicate a change in slope of line, however due to limited data this can not be confirmed.

6.7.13 Summary of Trial 4 Results

The key performance parameters of the manganese in tap water trial (Trial 4) are presented in Table 6.16.

Table 6.16: Trial 4 key performance parameters

	Min	Average	Max
Flow rates			
Average feed flow rate (l/hr)		9.6	
Average recirculation flow rate (l/hr)		11.3	
Feed Metals (mg/l)			
Calculated average Mn		172	
Retention Time (min)			
Stage I/ Stage II	9.13	13.8	16.8
pH (pH units)			
Influent	2.89	3.87	7.50
Stage I	7.59	8.22	8.76
Stage II	8.97	9.15	9.28
Effluent	8.32	8.97	9.15
Redox (mV)			
Influent		314	
Stage I		258	
Stage II		247	
Effluent		232	
Reagent Use			
Sodium hydroxide consumption (g/g)		1.81	
Sodium hydroxide consumption (mg/l)		339	
Sodium hydroxide efficiency (%)		77.9	
Flocculant dose (mg/l)		2.27	
Sludge Generation Rate (mg/l)		370	
Volumetric Recirculation Ratio	0.55	1.20	1.78
Mass Recirculation Ratio	20	173	376
Sludge Characteristics			
Reactor Solids (g/l)	0.50	12.1	35.8
2 Hour Settled Solids (g/l)	8.40	110	230
Recycle solids (g/l)	0.50	32.4	84.6
Initial settling Velocity (m/hr)	0.22	9.71	134
Final/ Initial solids ratio	6.41	10.9	25.0

During Trial 4, the Stage I reactor pH stabilising solids concentration appeared to be approximately 1.5% (w/v) (Figure 6.45), the lowest of all trials.

On the 28th March 2004, day 19 of the trial, the final/initial flocculation tank solids ratio was approximately 9.6. This was the highest ratio of all trials.

In comparison to the previous trials, by approximately day 17 a 4 % (w/v) solids sample settled at approximately 8 m/hr.

6.8 Trial 5 – Iron in Seawater

6.8.1 Trial 5 Introduction

The seawater trial was run between the 7th October 2003 and 3rd November 2003. Key stages during this trial were:

- 7th October 2003 to 9th October 2003, plant set up and commissioning;
- 10th October 2003 to 20th October 2003, build up of sludge mass and development of High Density Sludge (HDS) operating conditions;
- 20th October 2003 to 3rd November 2003, operation of the plant in HDS operating conditions.

The iron in seawater was trialled as there are a number of locations in the United Kingdom, e.g. Horden MWTP in County Durham (Coulton *et al.* 2004), where abandoned coal mines have highly saline water.

During the period between the 7th October 2003 and 16th October 2003, the plant desired iron concentration was 200mg/l. On the 17th October 2003, this was reduced to 100mg/l.

The actual average feed flow rate to the plant was 7.53 l/hr, whilst the actual average iron concentration was 225 mg/l.

During the early part of the trial, problems were experienced with the stability of the flocculated particles, probably due to the high chloride content of the seawater. As a result, the flocculant was changed on the 21st October 2003, from Magnafloc 155 to Magnafloc 4240 and then changed on the 24th October 2003 to Magnafloc 10 to produce a more robust floc structure.

The operating pH of the Stage II reactor during the trial was 8.5.

6.8.2 Plant Water Quality

Influent water quality samples were taken on the 12th October 2003 and the results are presented in Table 6.17 (analysis undertaken by Wheal Jane Laboratories).

Table 6.17: Trial 5 water quality analysis results - Total concentrations

Parameter	Influent (mg/l)	Effluent (mg/l)	Recirculated Sludge (g/l)	Stage II Reactor overflow (g/l)
Solids	192	73	74.8	22.6
Iron	26.2	0.06	32.2	9.33
Sulphate	2,290	2,040	3.20	2.50
Calcium	2,340	2,080	8.20	3.98

Further analysis of the influent was undertaken on the 24th September 2003 and 6th October 2003, indicating a dissolved iron concentration of 147 mg/l and 191 mg/l respectively.

Samples of the treated water discharged from the plant were taken for routine iron analysis. The results from these tests are summarised in Table 6.18 and indicate low residual dissolved iron concentrations. Unlike the manganese results in Trial 4, the dissolved iron concentrations do not improve as the trial proceeds.

Table 6.18: Trial 5 Discharge water quality results

Date	Dissolved Iron (mg/l)	pH
13 Oct 03	0.02	8.37 to 9.09
28 Oct 03	0.07	8.60
29 Oct 03	0.02	8.63
30 Oct 03	0.035	8.40 to 8.59

6.8.3 Plant Flows and Reactor Retention Time

The plant feed and recirculation flow rates are presented in Figure 6.54. The average feed rate during the trial was 7.5 l/hr whilst the recirculation flow rate averaged 6.1 l/hr. Due to problems during the trial with solids settleability as a result of poor floc structure, there was a need to regularly vary the plant feed. This also affected other operating parameters and particularly the mass recirculation ratio (see Section 6.8.11).

The reactor retention time during the seawater trial, Figure 6.54, varied between 15 and 40 minutes with average retention time being 24 minutes.

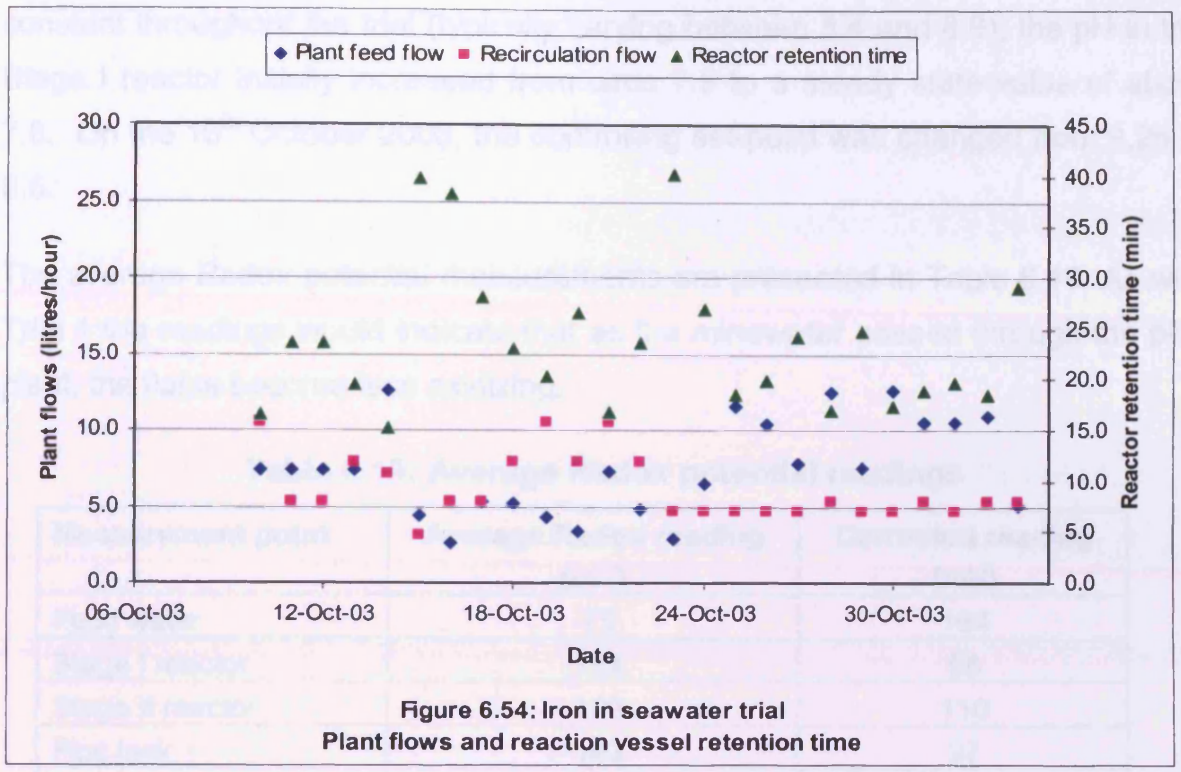


Figure 6.54: Iron in seawater trial
Plant flows and reaction vessel retention time

6.8.4 System pH, Redox Potential and Reactor Solids Concentration

The variations in the pH throughout the iron in seawater trial are summarised in Figure 6.55.

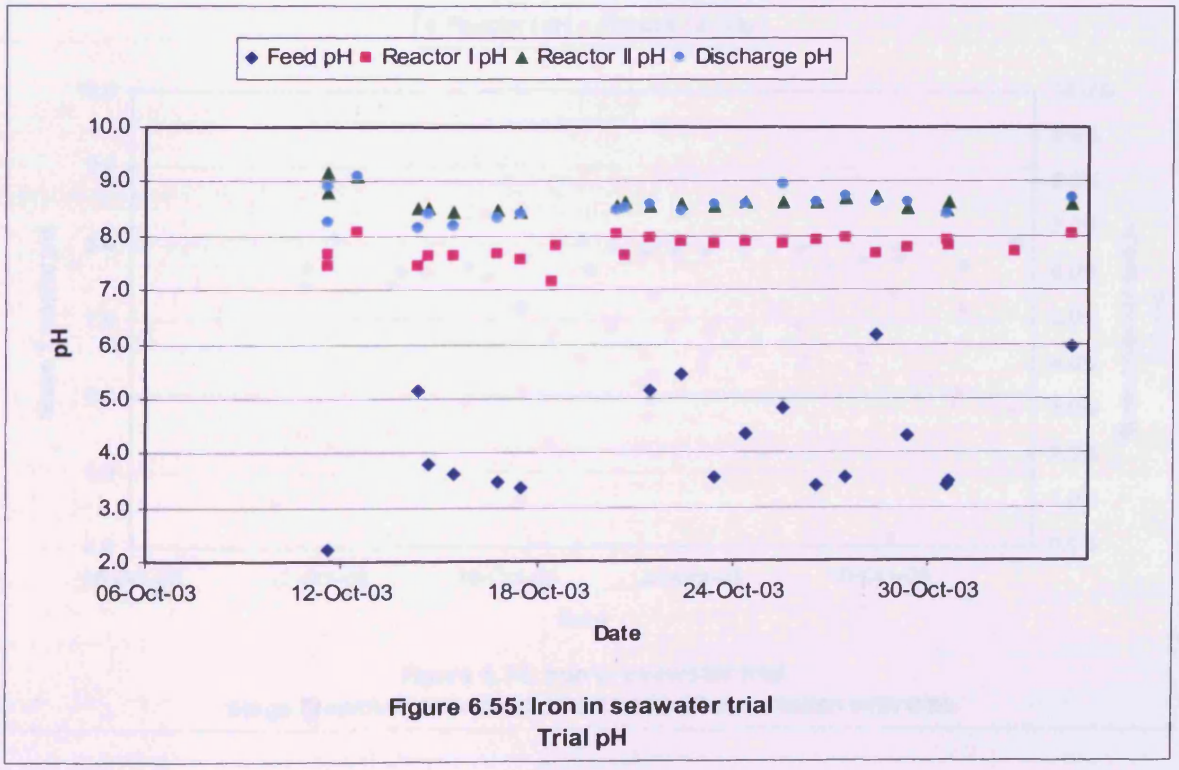


Figure 6.55: Iron in seawater trial
Trial pH

Figure 6.55 indicates that whilst the pH of the Stage II remained approximately

constant throughout the trial (typically varying between 8.4 and 8.6), the pH in the Stage I reactor initially increased from circa 7.5 to a steady state value of about 7.8. On the 16th October 2003, the controlling set-point was changed from 9.25 to 8.5.

The average Redox potential measurements are presented in Table 6.19. As with Trial 1 the readings would indicate that as the minewater passed through the pilot plant, the fluids become less oxidizing.

Table 6.19: Average Redox potential readings

Measurement point	Average Redox reading (mV)	Corrected reading (mV)
Feed water	-75	164
Stage I reactor	-184	58
Stage II reactor	-129	110
Floc tank	-143	97
Clarifier	-151	89
Recycle sludge	-152	88

The variation of Stage I reactor pH with the suspended solids concentration measured in the reactor is shown in Figure 6.56.

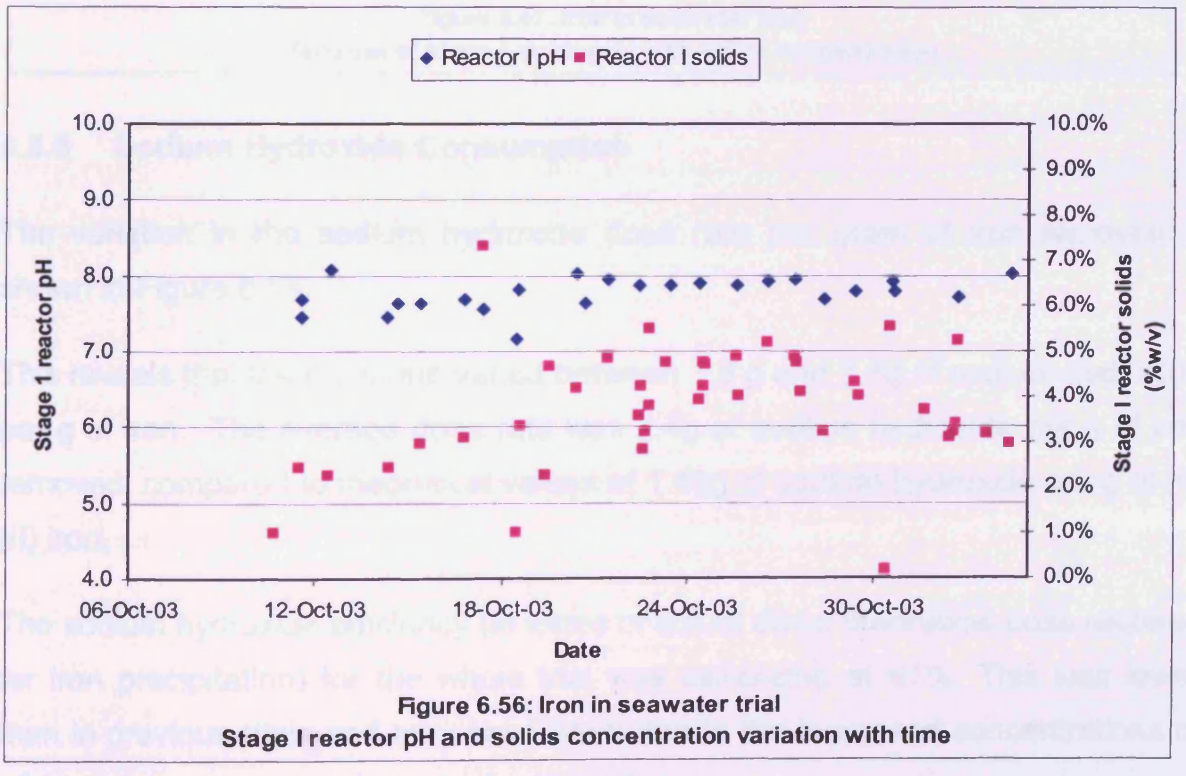


Figure 6.56: Iron in seawater trial
Stage I reactor pH and solids concentration variation with time

The variation in the Stage II reactor overflow solids concentration is shown in Figure 6.56. Due to the need to maintain an adequate flow velocity in the

recirculation line, higher solids concentrations than intended were maintained in the reactors, typically 4% w/v. This was reduced to 3% w/v for the last two days of the trial.

Figure 6.57 indicates that there is no discernable variation in the Stage I reactor pH, with solids concentration above 3.5% solids (w/v).

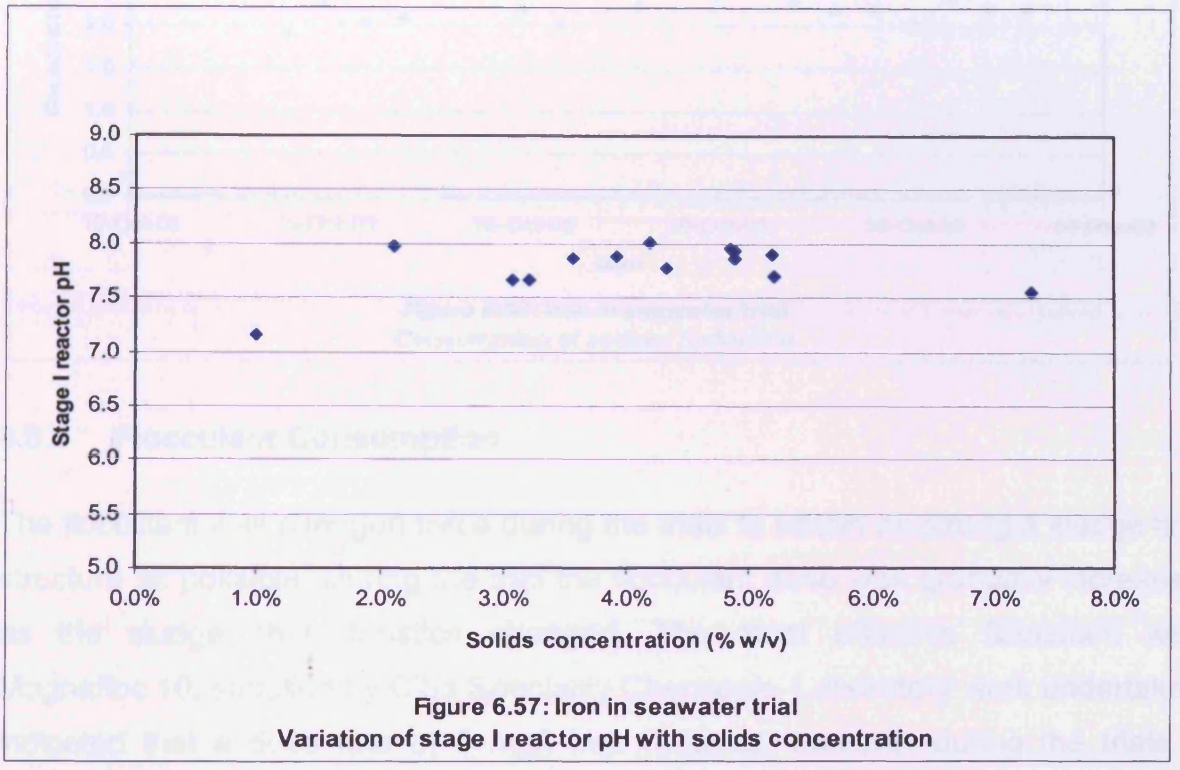


Figure 6.57: Iron in seawater trial
Variation of stage I reactor pH with solids concentration

6.8.5 Sodium Hydroxide Consumption

The variation in the sodium hydroxide dose rate per gram of iron removed is shown in Figure 6.58.

This reveals that the dose rate varied between 1.9 g and 3.1g of sodium hydroxide per g of iron. The average dose rate was 2.4g of sodium hydroxide per g of iron removed, compared to theoretical values of 1.43g of sodium hydroxide per g of Fe (II) iron.

The sodium hydroxide efficiency (in terms of actual dose/ theoretical dose required for iron precipitation) for the whole trial was calculated at 61%. This was lower than in previous trials and may have been due to the increased concentrations of other elements, e.g. sulphate, in the seawater.

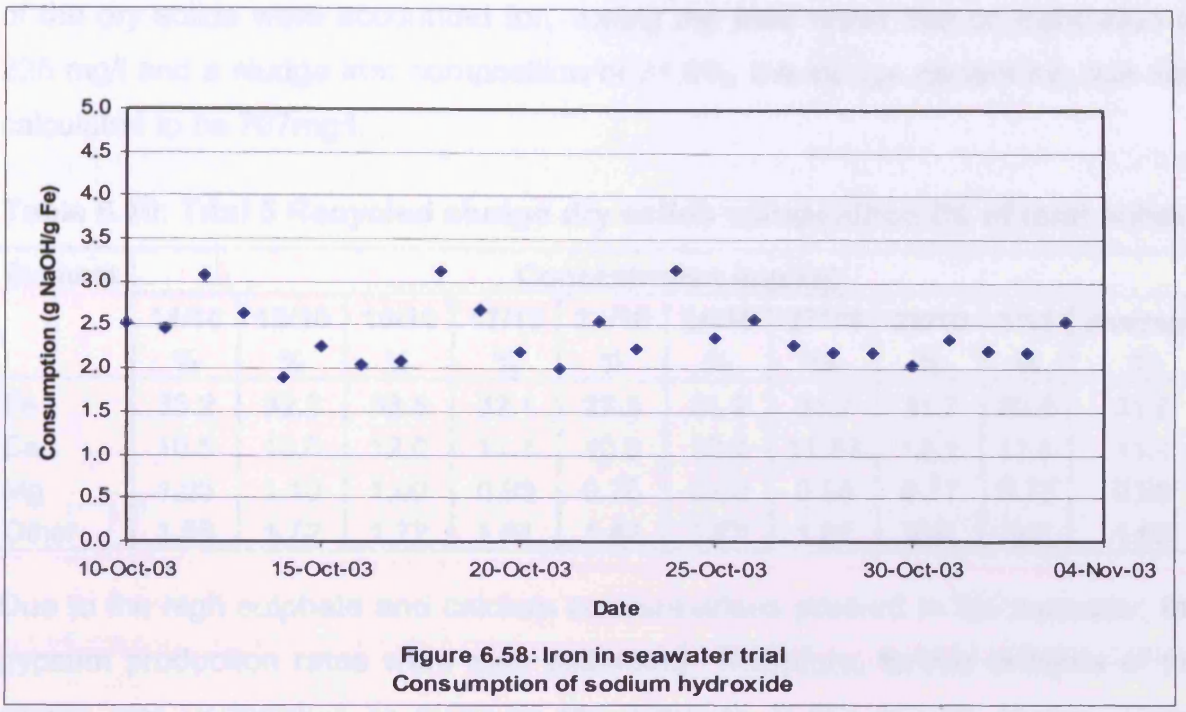


Figure 6.58: Iron in seawater trial
Consumption of sodium hydroxide

6.8.6 Flocculant Consumption

The flocculant was changed twice during the trials to obtain as strong a sludge floc structure as possible. During the trial the flocculant dose was gradually increased as the sludge characteristics changed. The most effective flocculant was Magnafloc 10, supplied by Ciba Speciality Chemicals. Laboratory work undertaken indicated that a dose rate of 5 mg/l was required, however during the trials a higher dose of 13.8 mg/l was required. This dose was higher than used during other trials and was likely to have been as a result of problems experienced with sludge floc stability.

6.8.7 Sludge Generation Rate

Analysis of the recycled sludge samples was undertaken throughout the seawater trial and the results are presented in Table 6.20.

The results indicate that the dry solids produced during the pilot plant trials contained on average 31.6% iron compared to a theoretical value of 52.3%, and resulted in 3.14g of sludge per g of iron removed. Assuming that the iron was removed as Fe (III) hydroxide, this would account for 60.4% of the dry solids. Additionally, assuming that the calcium and magnesium were removed as calcium carbonate and magnesium carbonate, this would account for 26.8 % and 3.1% of the dry solids respectively. With the 1.63% of other elements, approximately 92%

of the dry solids were accounted for. Using the feed water iron concentration of 225 mg/l and a sludge iron composition of 31.6%, the sludge generation rate was calculated to be 707mg/l.

Table 6.20: Trial 5 Recycled sludge dry solids composition (% of total solids)

Element	Concentration (mg/kg)									
	14/10 %	15/10 %	16/10 %	17/10 %	23/10 %	24/10 %	27/10 %	28/10 %	1/11 %	Average %
Fe	33.2	32.3	33.6	32.1	27.8	31.2	31.7	31.7	30.8	31.6
Ca	10.5	10.0	12.0	11.1	10.3	12.0	11.87	12.1	12.6	11.4
Mg	1.28	1.10	1.00	0.93	0.76	0.62	0.86	0.77	0.78	0.90
Other	1.56	1.72	1.72	1.61	1.42	1.57	1.81	N/A	N/A	1.63

Due to the high sulphate and calcium concentrations present in the seawater, the gypsum production rates were also estimated. Therefore, further analysis of the sludge was undertaken to measure the sulphate in the recycle sludge. These results are presented in Table 6.21.

Assuming that all sulphate present was present as gypsum, 1.95% of the dry solids would be gypsum. This would indicate that 94% of the solids have been accounted for and, allowing for experimental error, this is an acceptable mass balance.

The results from the above analysis indicate that little gypsum precipitation occurred, possibly due to complexing and/or suppression of calcium activity, due to the high chloride concentrations present in the seawater. This was also substantiated by analysis of the plant discharge on the 12th October 2003, when the calcium and sulphate concentrations were 2084 mg/l and 2045 mg/l respectively, which would indicate the discharge water was supersaturated with calcium sulphate even though little gypsum could be accounted for in the sludge.

Table 6.21: Trial 5 Final Sludge Composition

Element	Concentration (mg/kg)
Solids	158 (g/l)
Fe	30.7%
Ca	8.48%
SO_4	1.09%
OH	28.6%
CO_3	14.3%

Analysis undertaken by Wheal Jane Laboratories

6.8.8 Clarifier Underflow Characteristics

The variation in the clarifier underflow solids concentrations throughout the seawater trial is summarised in Figure 6.59 and shows that the clarifier underflow solids concentration varied between 2 and 18% (w/v).

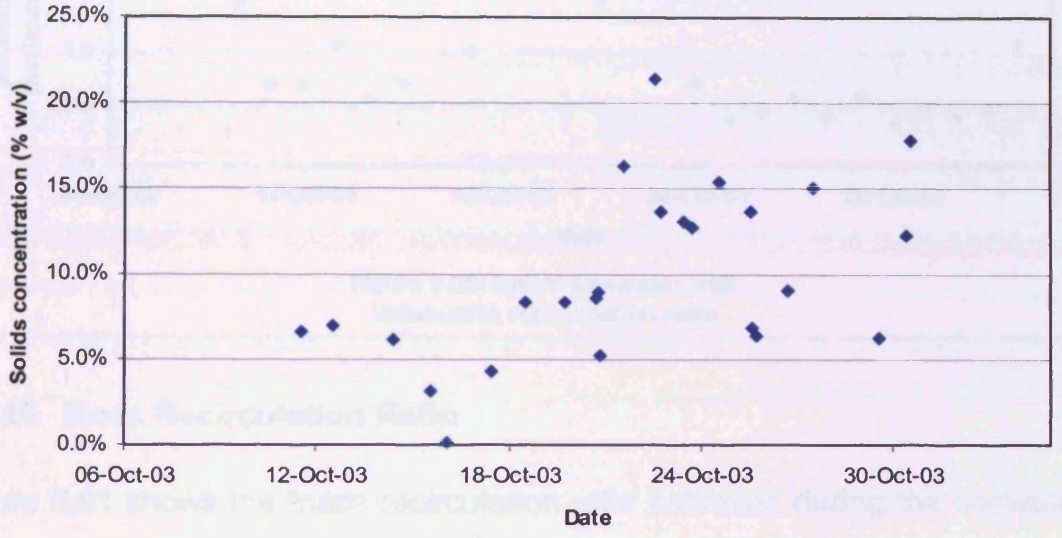


Figure 6.59: Iron in seawater trial
Variation in clarifier underflow solids concentration

6.8.9 Volumetric Recirculation Ratio

The variation of the volumetric recirculation ratio throughout the seawater trial is shown in Figure 6.60 and averaged 1.0.

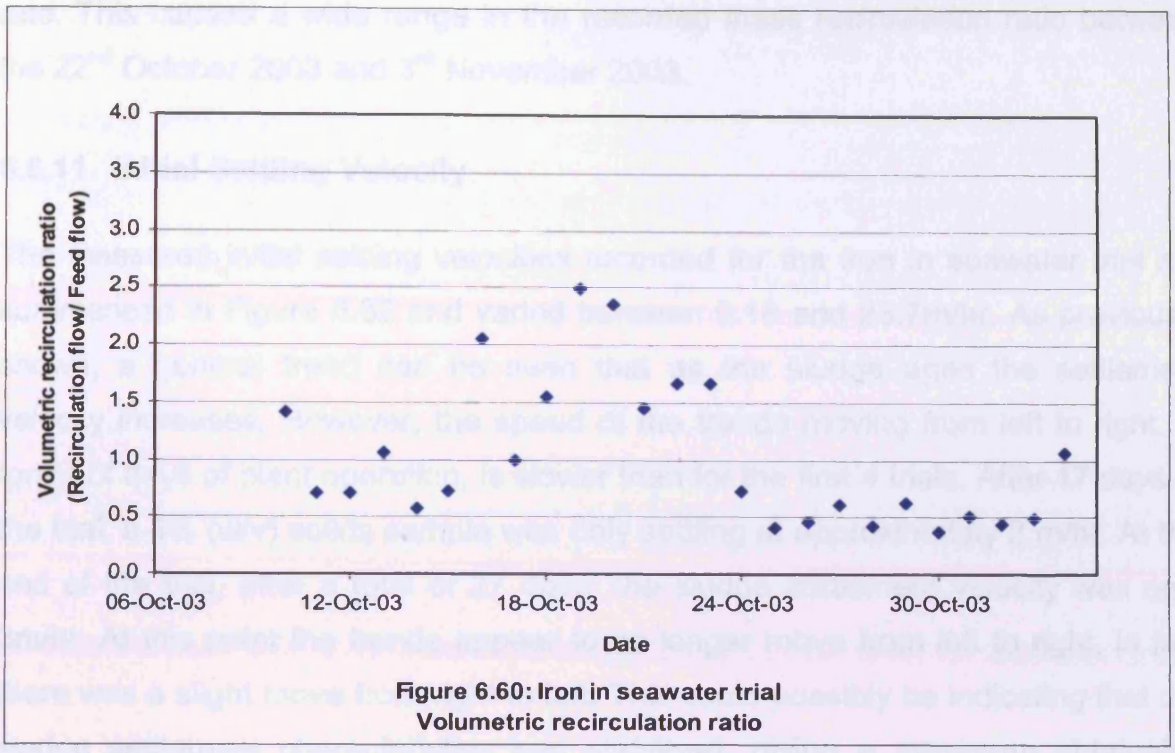


Figure 6.60: Iron in seawater trial
Volumetric recirculation ratio

6.8.10 Mass Recirculation Ratio

Figure 6.61 shows the mass recirculation ratio achieved during the seawater trial. The mass recirculation ratio varied between 38:1 and 250: 1, and the average recirculation ratio for the iron in seawater trial was 160:1.

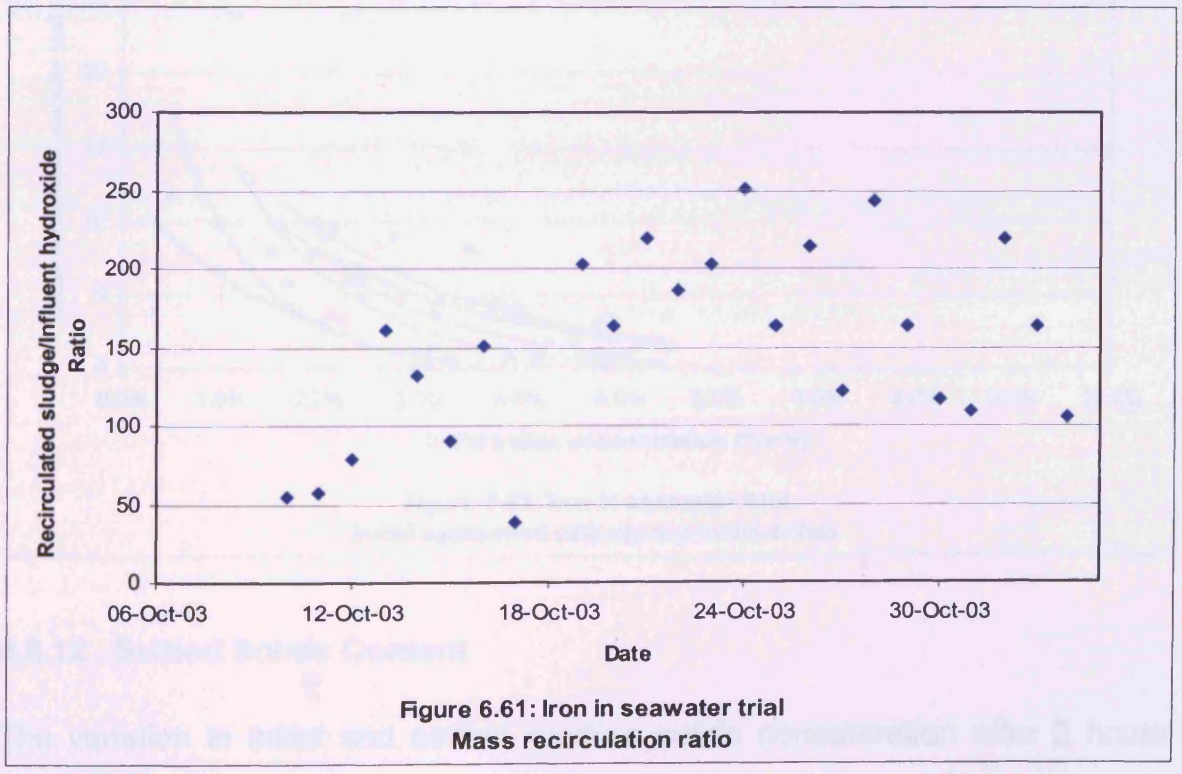


Figure 6.61: Iron in seawater trial
Mass recirculation ratio

As outlined in Section 6.8.4, there was a need to regularly vary the plant feed flow

rate. This caused a wide range in the recorded mass recirculation ratio between the 22nd October 2003 and 3rd November 2003.

6.8.11 Initial Settling Velocity

The measured initial settling velocities recorded for the iron in seawater trial are summarised in Figure 6.62 and varied between 0.18 and 23.7m/hr. As previously shown, a general trend can be seen that as the sludge ages the settlement velocity increases. However, the speed of the trends moving from left to right, in terms of days of plant operation, is slower than for the first 4 trials. After 17 days of the trial, a 4% (w/v) solids sample was only settling at approximately 2 m/hr. At the end of the trial, after a total of 27 days, the sludge settlement velocity was only 3m/hr. At this point the trends appear to no longer move from left to right, in fact there was a slight move from right to left. This could possibly be indicating that the sludge settlement characteristics had stabilised, giving a maximum obtainable settlement velocity for a 4% (w/v) solids sample of approximately 4 m/hr.

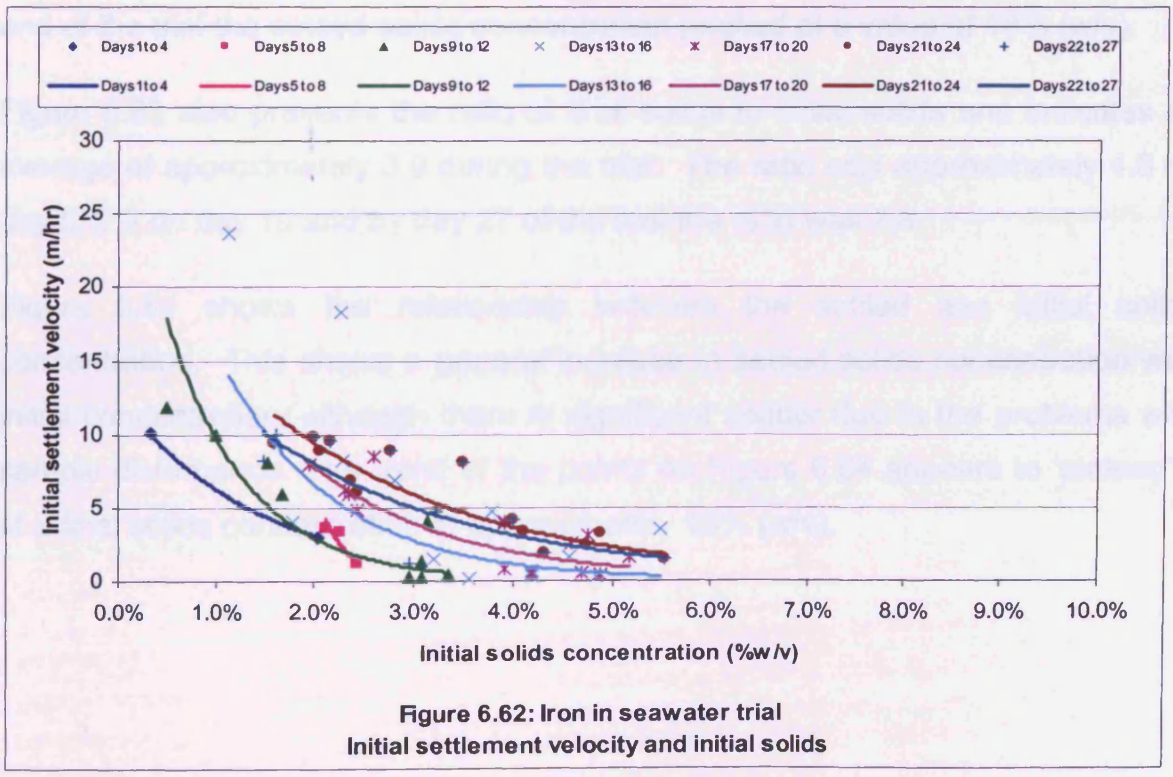


Figure 6.62: Iron in seawater trial
Initial settlement velocity and initial solids

6.8.12 Settled Solids Content

The variation in initial and settled mudline solids concentration after 2 hours is shown in Figure 6.63

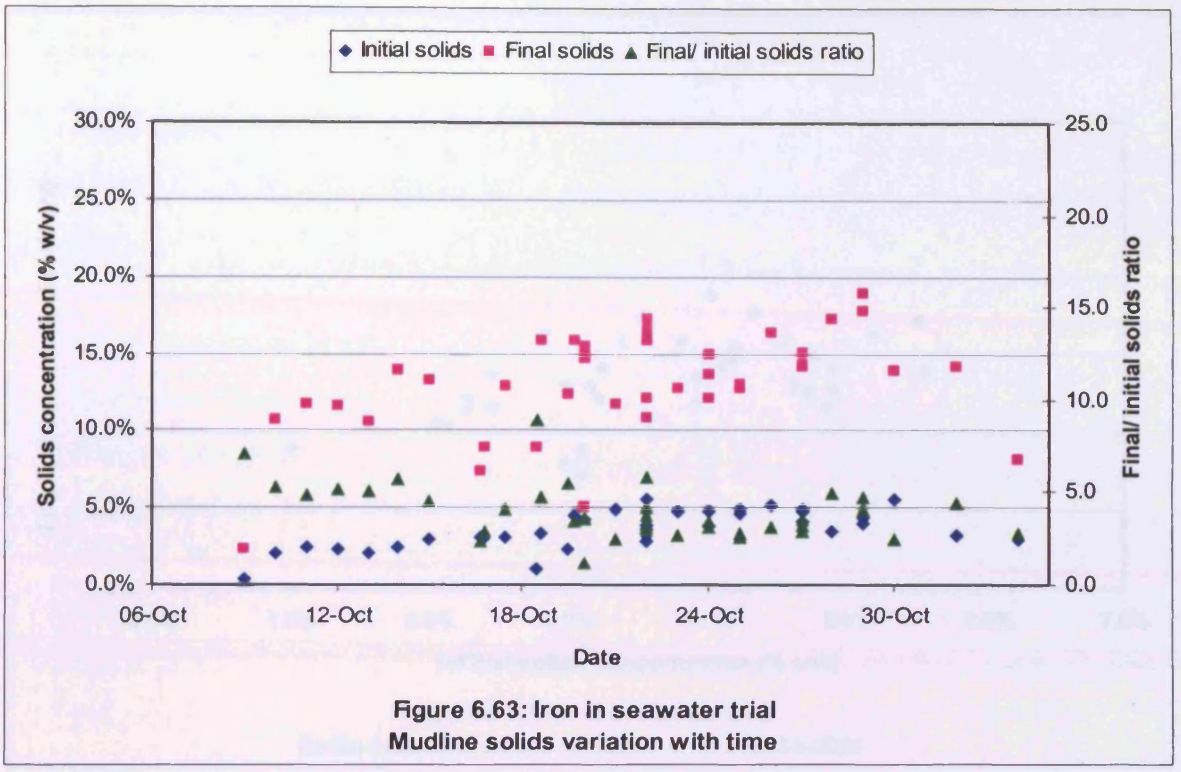


Figure 6.63: Iron in seawater trial
Mudline solids variation with time

The data shows a steady build up in the settled solids concentration and by the end of the trial the settled solids concentration peaked at a value of 18% (w/v).

Figure 6.63 also presents the ratio of final solids to initial solids and indicates an average of approximately 3.9 during the trial. The ratio was approximately 4.8 on day 5, 2.6 on day 19 and by day 27 of the trial the ratio was 2.8.

Figure 6.64 shows the relationship between the settled and initial solids concentration. This shows a general increase in settled solids concentration with initial concentration, although there is significant scatter due to the problems with sample disturbance. The trend of the points on Figure 6.64 appears to 'plateau's' at a final solids concentration of approximately 15% (w/v).

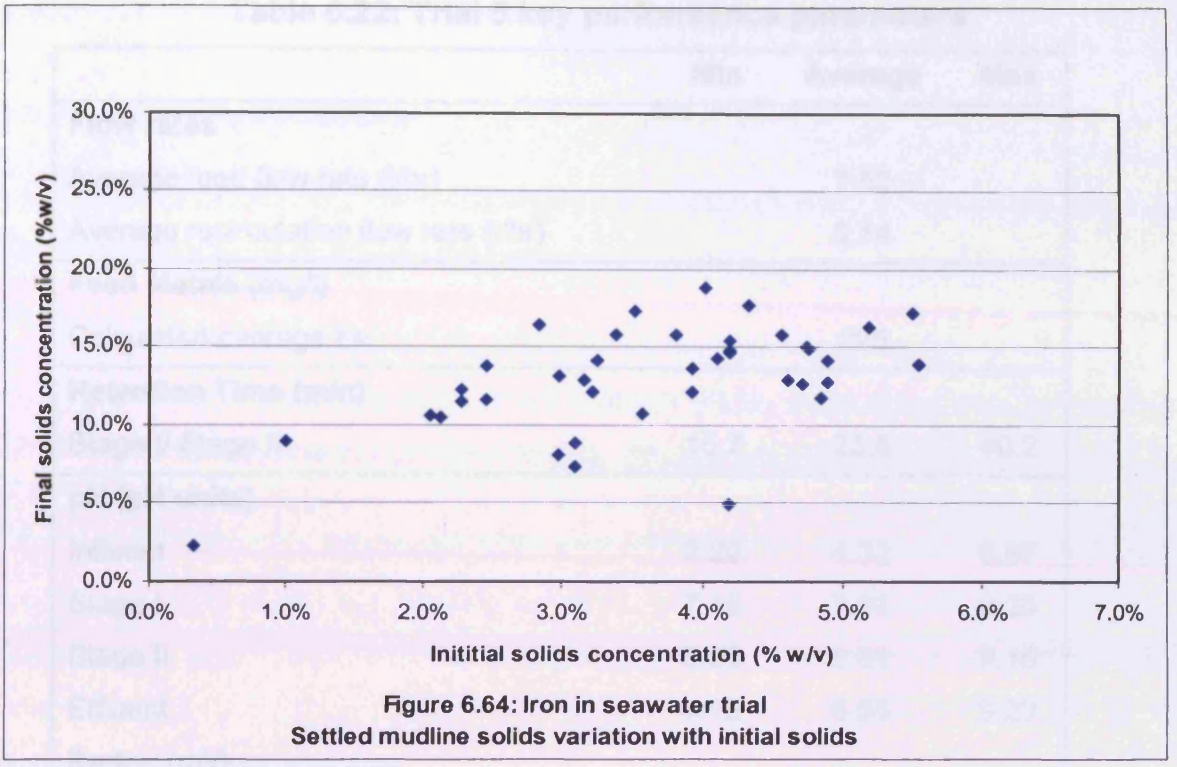


Figure 6.64: Iron in seawater trial
Settled mudline solids variation with initial solids

6.8.13 Summary of Trial 5 Results

The key performance parameters of the iron in seawater trial (Trial 5) are presented in Table 6.22.

During Trial 5, the Stage I reactor pH stabilising solids concentration appeared to be approximately 3.5% (w/v) (Figure 6.57).

On the 25th October 2003, day 19 of the trial, the final/initial flocculation tank solids ratio was approximately 2.6.

In comparison to the previous trials, after approximately day 17 a 4 % (w/v) solids sample settled at approximately 2 m/hr.

Table 6.22: Trial 5 key performance parameters

	Min	Average	Max
Flow rates			
Average feed flow rate (l/hr)		7.53	
Average recirculation flow rate (l/hr)		6.14	
Feed Metals (mg/l)			
Calculated average Fe		225	
Retention Time (min)			
Stage I/ Stage II	15.7	23.6	40.2
pH (pH units)			
Influent	2.22	4.32	6.97
Stage I	7.16	7.81	9.35
Stage II	8.36	8.61	9.16
Effluent	8.12	8.58	9.20
Redox (mV)			
Influent		164	
Stage I		58	
Stage II		110	
Effluent		89	
Reagent Use			
Sodium hydroxide consumption (g/g)		2.36	
Sodium hydroxide consumption (mg/l)		531	
Sodium hydroxide efficiency (%)		60.5	
Flocculant dose (mg/l)		13.8	
Sludge Generation Rate (mg/l)		707	
Volumetric Recirculation Ratio	0.37	1.02	2.48
Mass Recirculation Ratio	38	160	403
Sludge Characteristics			
Reactor Solids (g/l)	3.30	36.3	55.4
2 Hour Settled Solids (g/l)	2.34	130	189
Recycle solids (g/l)	0.90	96.8	276
Initial settling Velocity (m/hr)	0.18	4.75	23.7
Final/ Initial solids ratio	1.19	3.93	8.93

6.9 Trial 6 – Mixed Metals in Tap Water

6.9.1 Trial 6 Introduction

The mixed metals in tap water trial was run between the 11th February 2004 and 05th March 2004. Key stages during this trial were:

- 11th February 2004, plant set up and commissioning;
- 10th February 2004 to 05th March 2004, build up of sludge mass and development of High Density Sludge (HDS) operating conditions.

The mixed metals in tap water trial was undertaken as there are a number of locations world wide, e.g. Britannia Mine, Vancouver, Canada (see Table 2.1 Section 2.2) and Parys Mountain, Anglesey, Wales (see Table 2.1 Section 2.2), where abandoned mines contain a complex of various metals and not just iron in the acid minewater drainage.

The average feed flow to the plant during the trials was 7.75 l/hr, whilst the average total metal concentration was 172.3mg/l (made up of 31.3mg/l of zinc, 51.4mg/l of iron, 15.4mg/l of manganese, 46.0mg/l of aluminium and 28.2mg/l of copper).

6.9.2 Plant Water Quality

Results of water quality sample analysis of the feed water during the trial are presented in Table 6.23. In comparison to previous trials, a metal mix was fed to the plant instead of a single metal solution, with an average total metal concentration of 172 mg/l, which was comparable to the feed metal concentration of previous trials.

Water quality samples of the discharge water were taken during the trial. Results from these are presented in Table 6.24 (total metals) and Table 6.25 (dissolved metals). As with previous trials, the treatment objective was to reduce the discharge metal concentrations to below 1 mg/l.

Table 6.23: Trial 6 feed water quality results – Total concentrations

Date	Zn (mg/l)	Fe (mg/l)	Mn (mg/l)	Al (mg/l)	Cu (mg/l)	Ca (mg/l)	Mg (mg/l)	SO4 (mg/l)	Ba (mg/l)	K (mg/l)	Na (mg/l)
17 Feb 04	31.9	74.9	13.9	69.5	32.7	327	96.9				
19 Feb 04	31.0	84.0	14.4	64.3	27.9	320	93.6				
23 Feb 04	28.7	18.3	11.3	24.7	28.7	276	85.2				
27 Feb 04	26.1	10.6	10.9	12.1	26.9	352	79.9	690			
29 Feb 04	25.7	10.3	10.8	11.4	25.4	309	81.1		0.2	31.1	148
01 Mar 04	34.4	25.4	28.0	18.1	12.6	342	92.9		0.4	15.2	132
03 Mar 04	37.8	33.2	31.5	27.2	28.6	397	109		0.2	27.6	165
04 Mar 04	35.2	13.3	16.0	6.4	25.9	180	83.2		0.2	24.8	154
05 Mar 04	37.6	16.0	16.4	10.5	27.9	184	83.7		0.4	28.2	160
Max	**37.8**	**84.0**	**31.5**	**69.5**	**32.7**	**397**	**109**	**690**	**0.4**	**31.1**	**165**
Average	**32.0**	**31.8**	**17.0**	**27.1**	**26.3**	**299**	**89.5**	**690**	**0.3**	**25.4**	**152**
Min	**25.7**	**10.3**	**10.8**	**6.4**	**12.6**	**180**	**79.9**	**690**	**0.2**	**15.2**	**132**

Table 6.24: Trial 6 discharge water quality results - Total concentrations

Date	Zn (mg/l)	Fe (mg/l)	Mn (mg/l)	Al (mg/l)	Cu (mg/l)	Ca (mg/l)	Mg (mg/l)	SO4 (mg/l)	Ba (mg/l)	K (mg/l)	Na (mg/l)
17 Feb 04	15.1	0.6	10.9	<0.1	0.9	436	72.5				
19 Feb 04	13.6	7.3	11.5	4.6	5.0	441	78.4				
23 Feb 04	22.0	0.6	10.4	1.3	2.5	323	77.6				
27 Feb 04	<0.1	0.3	4.3	0.3	0.4	377	71.6	610			
29 Feb 04	0.3	0.5	2.3	0.3	0.4	341	61.3		<0.1	26.9	125
01 Mar 04	0.2	0.4	11.7	0.4	0.3	420	77.3		0.1	14.9	148
03 Mar 04	0.2	0.2	12.0	0.7	0.1	416	81.0		0.1	22.4	148
04 Mar 04	0.6	0.2	4.1	0.2	<0.1	267	71.2		0.1	22.7	145
05 Mar 04	0.1	0.1	4.1	0.3	0.1	278	71.8		0.1	24.5	153
Max	**22.0**	**7.3**	**12.0**	**4.6**	**5.0**	**441**	**81.0**	**610**	**0.1**	**26.9**	**153**
Average	**5.8**	**1.1**	**7.9**	**0.9**	**1.1**	**366**	**73.6**	**610**	**0.1**	**22.3**	**144**
Min	**<0.1**	**0.1**	**2.3**	**<0.1**	**<0.1**	**267**	**61.3**	**610**	**<0.1**	**14.9**	**125**

Note <0.1 indicates less than detection limit

Table 6.25: Trial 6 discharge water quality results - Dissolved concentrations

Date	Zn (mg/l)	Fe (mg/l)	Mn (mg/l)	Mg (mg/l)	Al (mg/l)	Cu (mg/l)	Ca (mg/l)	Ba (mg/l)	K (mg/l)	Na (mg/l)
17 Feb 04										
19 Feb 04	13.4	0.2	11.6	74.8	1.2	2.5	438			
23 Feb 04	24.4	0.5	10.9	77.8	1.3	4.3	319			
04 Mar 04	0.6	0.2	4.1	71.2	0.2	<0.1	267	0.1	22.7	145
05 Mar 04	0.1	<0.1	3.8	70.0	0.3	<0.1	277	0.1	25.3	150
Max	**24.4**	**0.5**	**11.6**	**77.8**	**1.3**	**4.3**	**438**	**0.1**	**25.3**	**150**
Average	**9.6**	**0.2**	**7.6**	**73.4**	**0.8**	**1.7**	**325**	**0.1**	**24.0**	**148**
Min	**0.1**	**<0.1**	**3.8**	**70.0**	**0.2**	**<0.1**	**267**	**0.1**	**22.7**	**145**

Note <0.1 indicates less than detection limit

6.9.3 Plant Flows and Reactor Retention Time

The plant feed and recirculation flow rates are presented in Figure 6.65. The

average feed rate during the trial was 7.5 l/hr, whilst the recirculation flow rate averaged 11.7 l/hr.

The reactor retention time during the mixed metal trial, presented in Figure 6.65, varied between 12.8 and 19.8 minutes, with an average of 15.6 minutes.

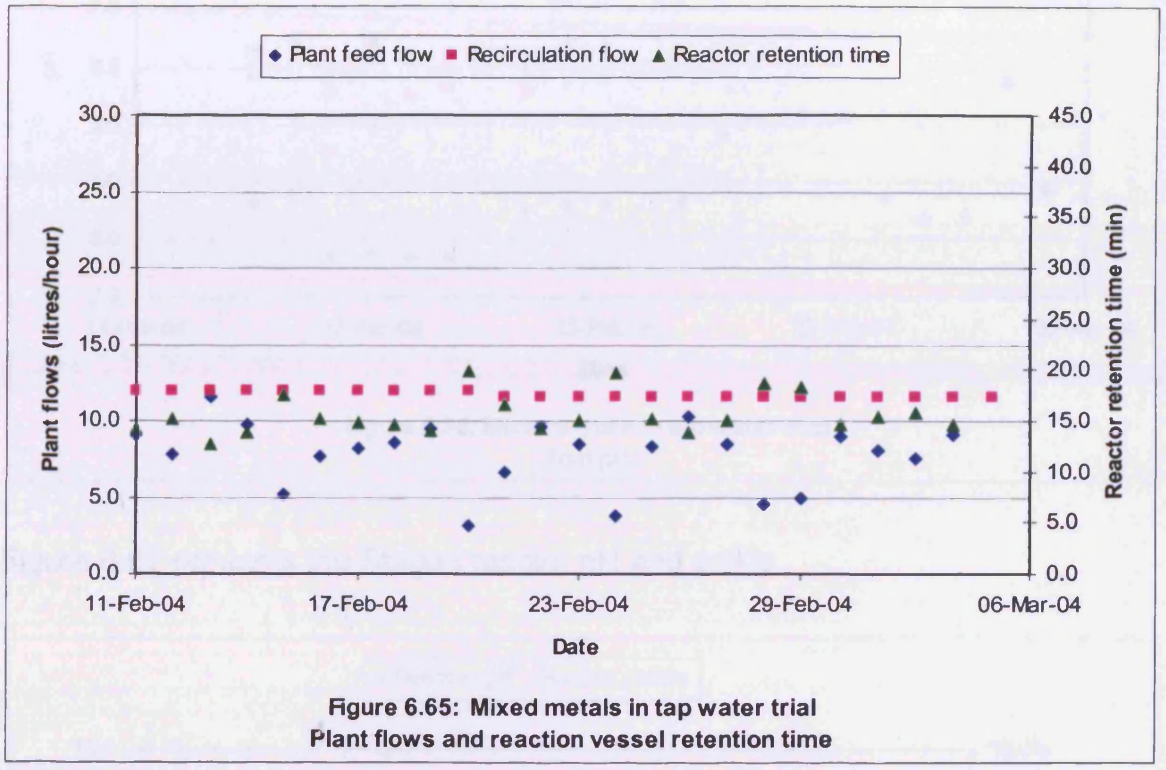


Figure 6.65: Mixed metals in tap water trial
Plant flows and reaction vessel retention time

6.9.4 System pH, Redox Potential and Reactor Solids Concentration

The variation of pH within the plant throughout the mixed metals trial is presented in Figure 6.66.

The average Redox potential measurements are presented in Table 6.26.

Table 6.26: Trial 6 average Redox potential readings

Measurement point	Average Redox reading (mV)	Corrected reading (mV)
Feed water	29	269
Stage I reactor	-58	182
Stage II reactor	-59	181
Floc tank	-61	179
Clarifier	-57	183
Recycle sludge	-61	179

The set-point in the pH controller was changed from 6.5 to 9.0 on the 24th February 2004.

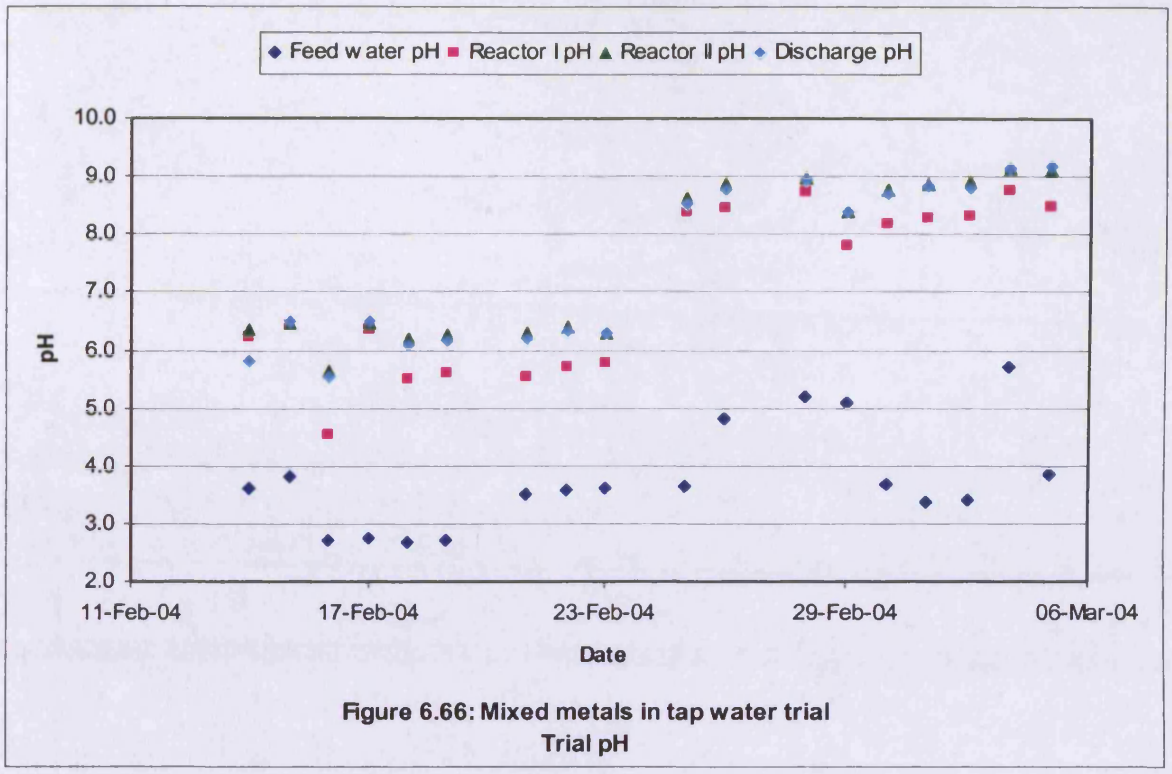


Figure 6.66: Mixed metals in tap water trial
Trial pH

Figure 6.67 presents the Stage I reactor pH and solids.

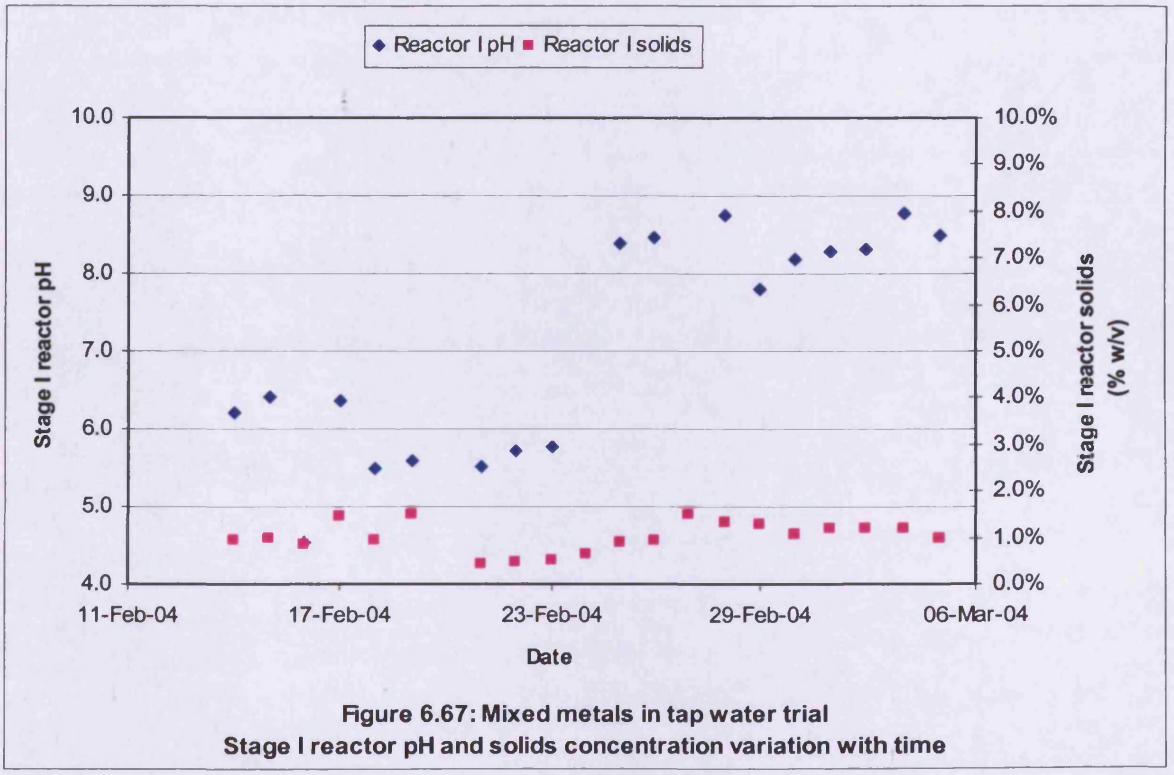


Figure 6.67: Mixed metals in tap water trial
Stage I reactor pH and solids concentration variation with time

The variation of Stage I reactor pH with the suspended solids concentration is shown in Figure 6.68. Due to limited variation in the Stage I reactor solids concentration, it is not possible to conclude at what solids concentration the Stage I reactor pH stabilised.

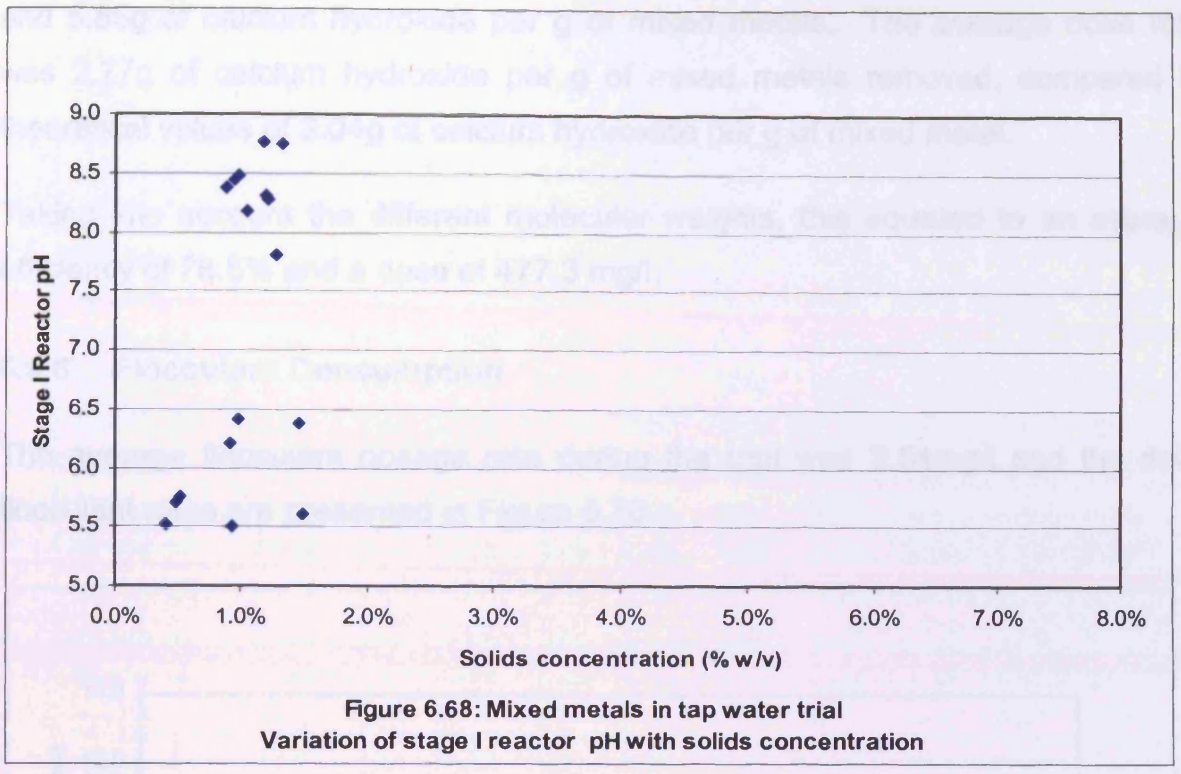


Figure 6.68: Mixed metals in tap water trial
Variation of stage I reactor pH with solids concentration

6.9.5 Calcium Hydroxide Consumption

The variation in the calcium hydroxide dose rate per g of metal removed is shown in Figure 6.69.

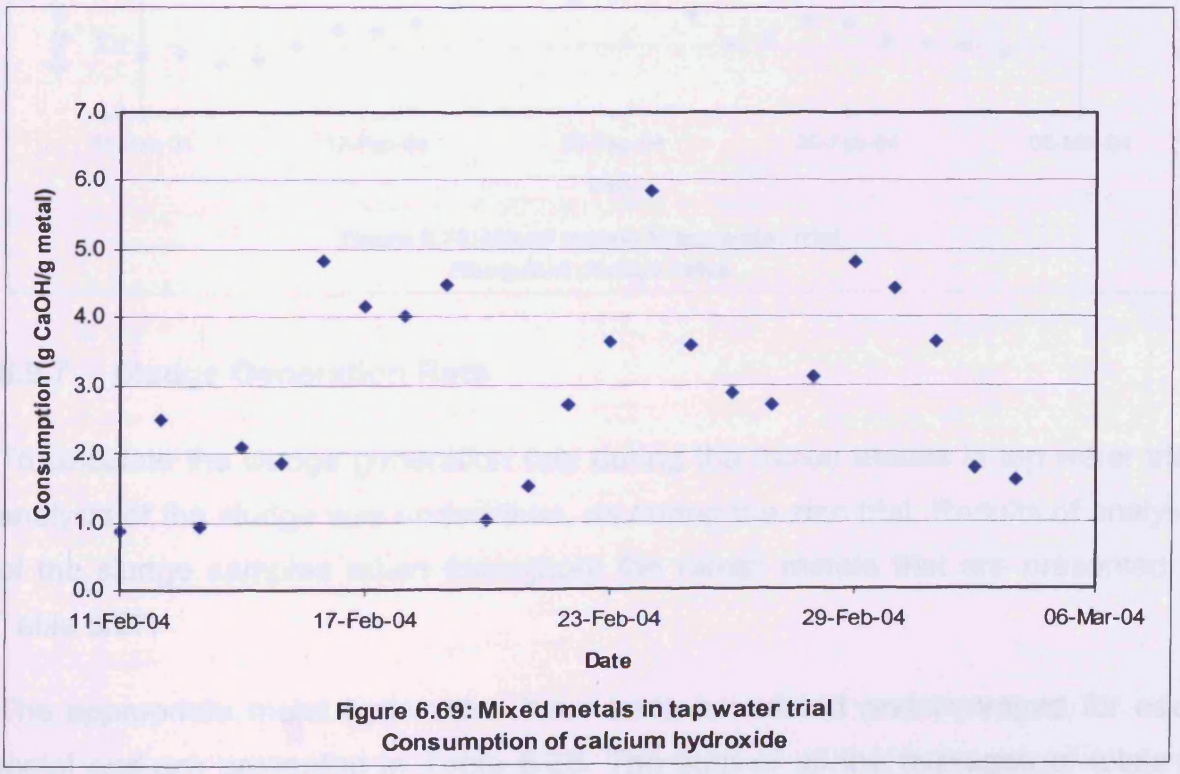


Figure 6.69: Mixed metals in tap water trial
Consumption of calcium hydroxide

During the trial, a total of 743.5g of mixed metals were treated, using a total of 2059g of calcium hydroxide. This reveals that the dose rate varied between 1.59g

and 5.85g of calcium hydroxide per g of mixed metals. The average dose rate was 2.77g of calcium hydroxide per g of mixed metals removed, compared to theoretical values of 2.04g of calcium hydroxide per g of mixed metal.

Taking into account the different molecular weights, this equated to an average efficiency of 73.5% and a dose of 477.3 mg/l.

6.9.6 Flocculant Consumption

The average flocculant dosage rate during the trial was 2.54mg/l and the daily flocculant rates are presented in Figure 6.70.

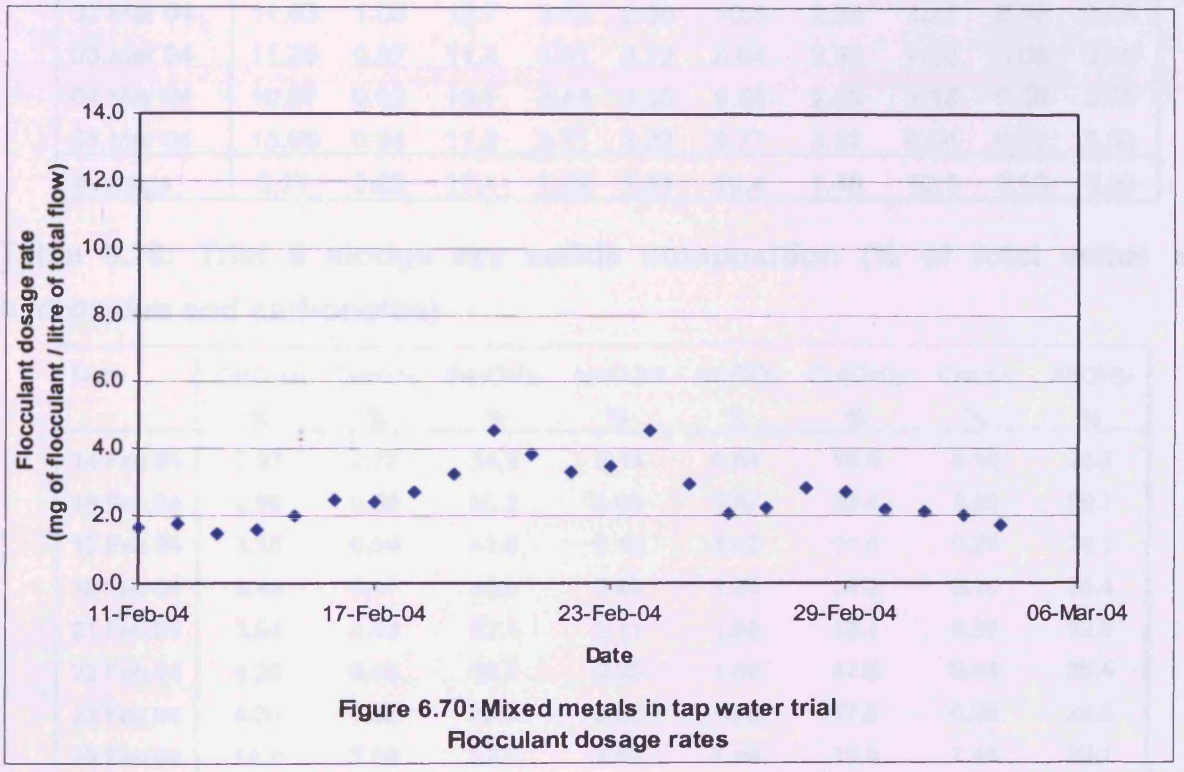


Figure 6.70: Mixed metals in tap water trial Flocculant dosage rates

6.9.7 Sludge Generation Rate

To calculate the sludge generation rate during the mixed metals in tap water trial, analysis of the sludge was undertaken, as during the zinc trial. Results of analysis of the sludge samples taken throughout the mixed metals trial are presented in Table 6.27.

The appropriate metal hydroxides have been calculated and averaged for each metal and are presented in Table 6.28. The sum of all the averages of totals is 102.6%; though over 100%, this is an acceptable mass balance as this is within analytical error.

Table 6.27: Trial 6 Sludge dry solids composition (% of total solids)

Date	Zn	Ba	Fe	Mn	Mg	Cu	Ca	Al	Na	K
	%	%	%	%	%	%	%	%	%	%
14 Feb 04	1.88	0.45	28.4	0.08	0.24	12.0	0.06	9.79	0.31	0.10
16 Feb 04	1.74	0.43	31.5	0.05	0.25	12.6	0.03	10.3	0.32	0.13
18 Feb 04	2.09	0.37	21.8	0.08	0.29	7.14	0.11	9.73	0.29	0.09
19 Feb 04	2.29	0.29	23.5	0.06	0.35	8.77	0.04	12.3	0.30	0.08
21 Feb 04	2.59	0.27	16.8	0.07	0.39	8.44	0.15	11.4	0.26	0.04
22 Feb 04	2.75	0.28	20.8	0.13	0.47	10.8	0.18	13.3	0.26	0.04
23 Feb 04	2.99	0.24	17.2	0.14	0.55	10.9	0.15	13.3	0.23	0.03
26 Feb 04	9.29	1.59	11.5	1.62	2.14	12.2	2.99	10.1	0.12	0.04
27 Feb 04	8.95	2.55	14.4	1.23	1.92	13.3	2.35	10.1	0.13	0.06
01 Mar 04	12.36	2.14	12.0	2.73	2.41	11.0	2.78	8.79	0.11	0.06
02 Mar 04	11.63	1.09	12.7	3.63	2.68	10.5	2.85	10.1	0.10	0.06
03 Mar 04	11.39	0.87	11.4	3.91	3.12	8.64	2.55	8.26	0.06	0.06
04 Mar 04	10.87	0.92	10.1	3.48	3.05	9.58	2.89	7.16	0.08	0.05
05 Mar 04	13.95	0.94	11.8	3.71	3.22	9.77	3.32	6.64	0.07	0.06
Average	6.77	0.89	17.4	1.49	1.51	10.4	1.46	10.1	0.19	0.06

Table 6.28: Trial 6 sludge dry solids composition (% of total solids as hydroxides and carbonates)

Date	$Zn(OH)_2$	$BaSO_4$	$Fe(OH)_3$	MnOOH	$MgCO_3$	$Cu(OH)_2$	$CaCO_3$	$Al(OH)_3$
	%	%	%	%	%	%	%	%
14 Feb 04	2.87	0.72	54.3	0.13	0.84	19.5	0.16	28.3
16 Feb 04	2.66	0.69	60.2	0.09	0.86	20.4	0.06	29.7
18 Feb 04	3.18	0.59	41.6	0.12	1.03	11.6	0.28	28.1
19 Feb 04	3.49	0.47	45.0	0.09	1.24	14.2	0.10	35.4
21 Feb 04	3.94	0.43	32.1	0.11	1.38	13.7	0.37	32.9
22 Feb 04	4.20	0.45	39.7	0.20	1.65	17.5	0.44	38.4
23 Feb 04	4.56	0.39	32.9	0.22	1.93	17.6	0.38	38.5
26 Feb 04	14.2	2.58	22.0	2.60	7.49	19.8	7.48	29.1
27 Feb 04	13.6	4.14	27.5	1.97	6.73	21.6	5.87	29.3
01 Mar 04	18.8	3.47	22.9	4.37	8.45	17.9	6.96	25.4
02 Mar 04	17.7	1.77	24.2	5.81	9.37	17.0	7.12	29.2
03 Mar 04	17.4	1.41	21.7	6.26	10.9	14.0	6.37	23.9
04 Mar 04	16.6	1.49	19.3	5.57	10.7	15.5	7.22	20.7
05 Mar 04	21.3	1.52	22.6	5.93	11.3	15.8	8.30	19.2
Average	10.3	1.44	33.3	2.39	5.27	16.8	3.65	29.1

Table 6.29 presents the calculated sludge generation rate for the trial using the percentage of iron, copper, zinc aluminium and manganese in the sludge. These were averaged to calculate the trial solids generation rate of 286 mg of solids per litre of minewater treated.

Table 6.29: Trial 6 calculated sludge generation rate

Element	% of Solids (%)	Average feed (mg/l)	Sludge generation (mg/l)
$Zn(OH)_2$	10.3	31.3	304
$Fe(OH)_3$	33.3	51.4	154
MnOOH	2.39	15.4	644
$Cu(OH)_2$	16.8	28.2	167
$Al(OH)_3$	29.1	46.0	158
Average sludge generation rate			286

6.9.8 Clarifier Underflow Characteristics

The variation in the clarifier underflow solids concentrations throughout the mixed metals Trial is summarised in Figure 6.71. The clarifier underflow solids concentration varied between 0 and 4.96% (w/v).

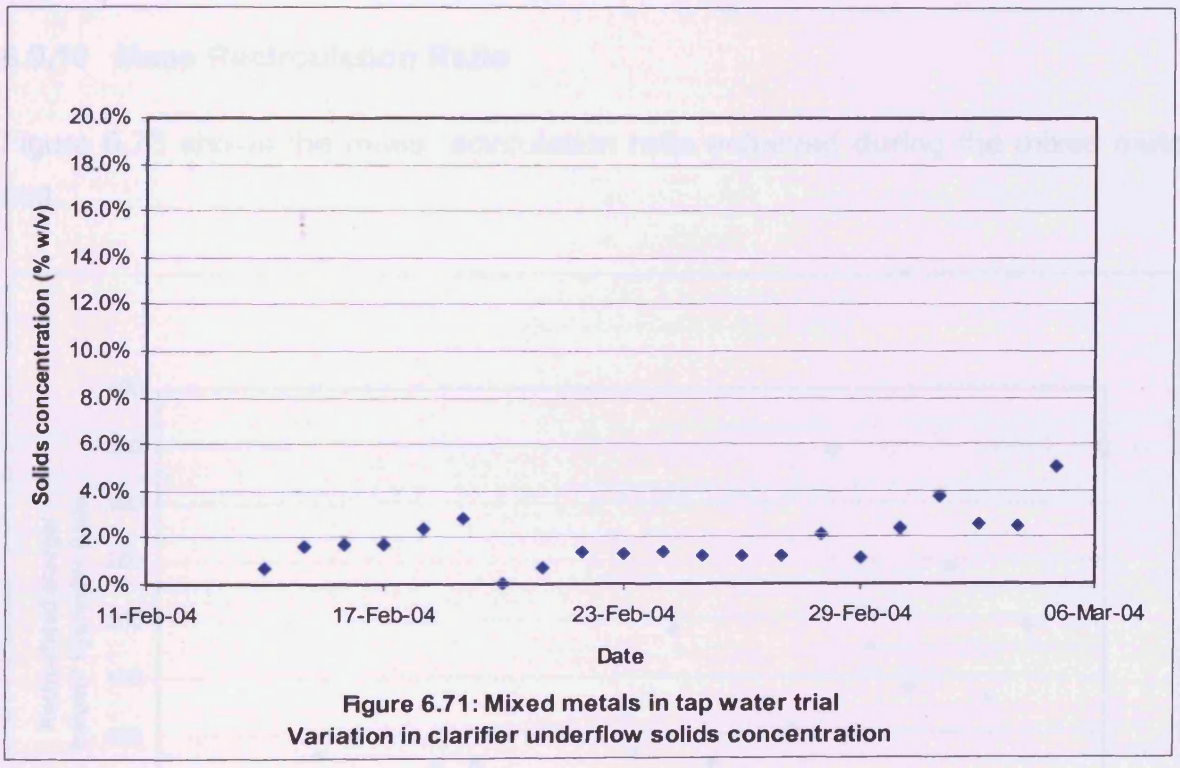


Figure 6.71: Mixed metals in tap water trial
Variation in clarifier underflow solids concentration

6.9.9 Volumetric Recirculation Ratio

The variation of the volumetric recirculation ratio throughout the aluminium trial is shown in Figure 6.72 and averaged 1.68.

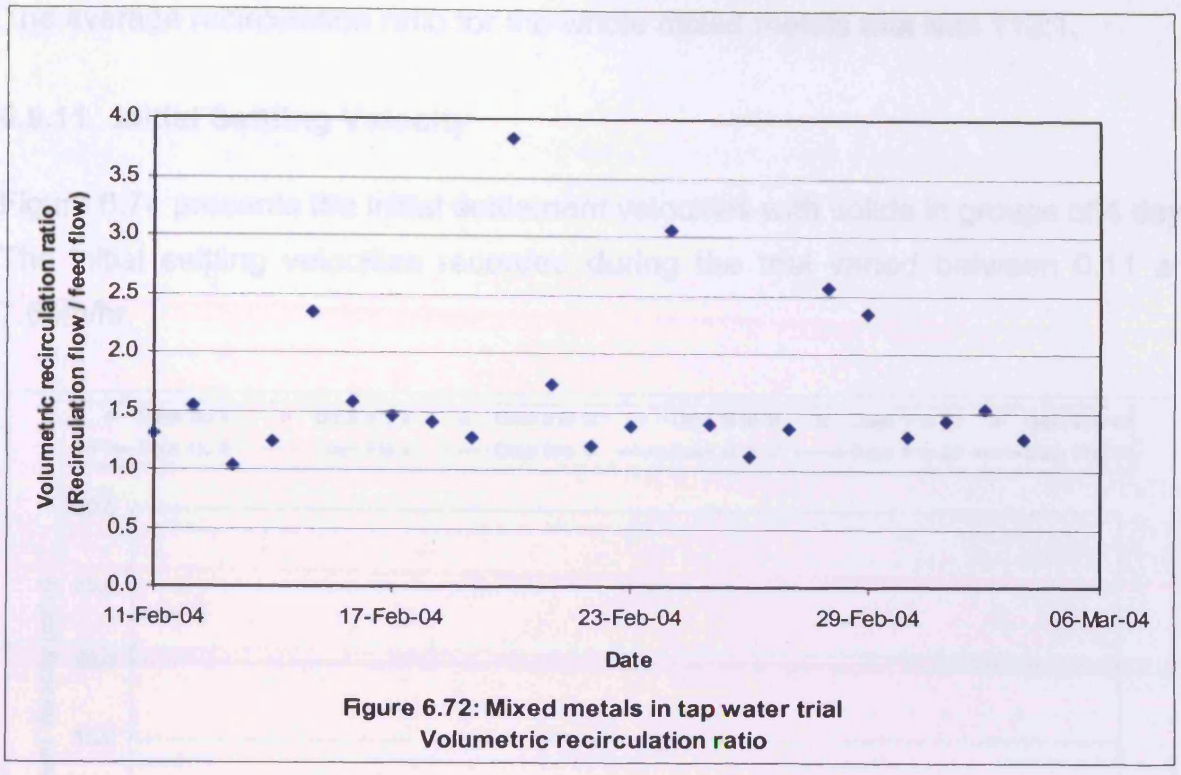


Figure 6.72: Mixed metals in tap water trial
Volumetric recirculation ratio

6.9.10 Mass Recirculation Ratio

Figure 6.73 shows the mass recirculation ratio achieved during the mixed metals trial.

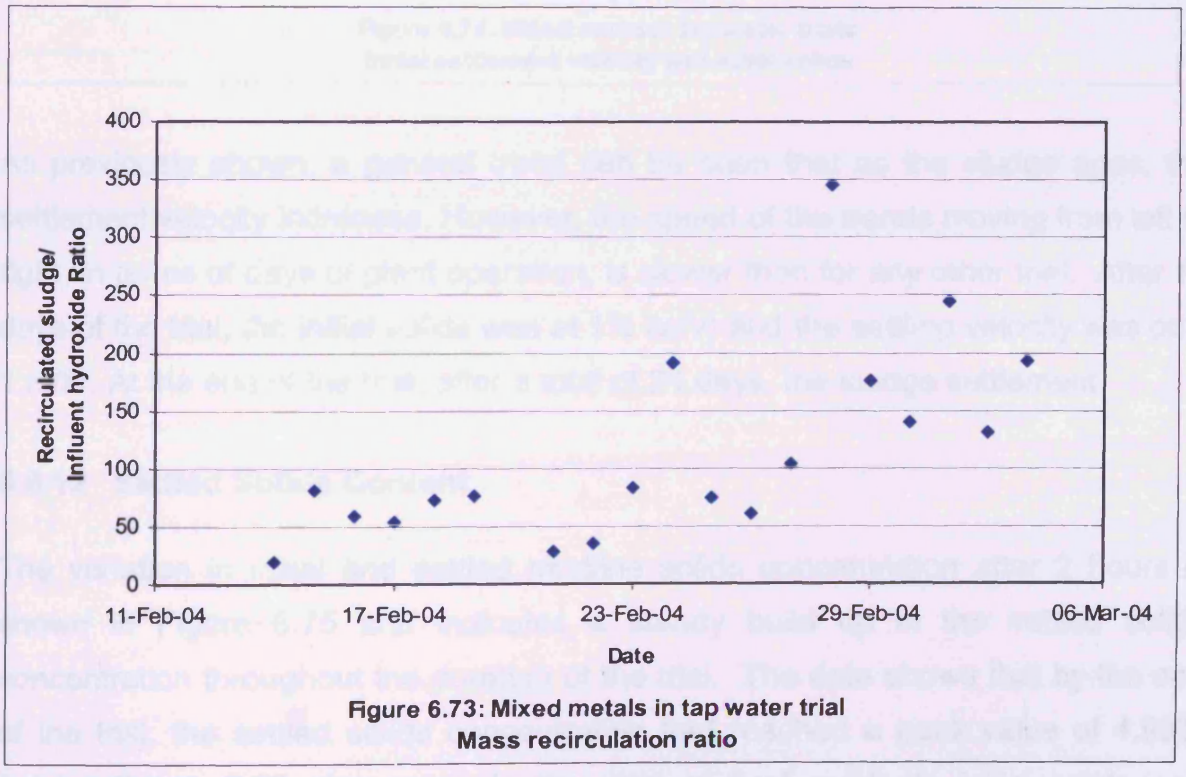


Figure 6.73: Mixed metals in tap water trial
Mass recirculation ratio

The mass recirculation ratio varied between 19:1 and 345:1 during the whole trial.

The average recirculation ratio for the whole mixed metals trial was 113:1.

6.9.11 Initial Settling Velocity

Figure 6.74 presents the initial settlement velocities with solids in groups of 4 days. The initial settling velocities recorded during the trial varied between 0.11 and 7.65m/hr.

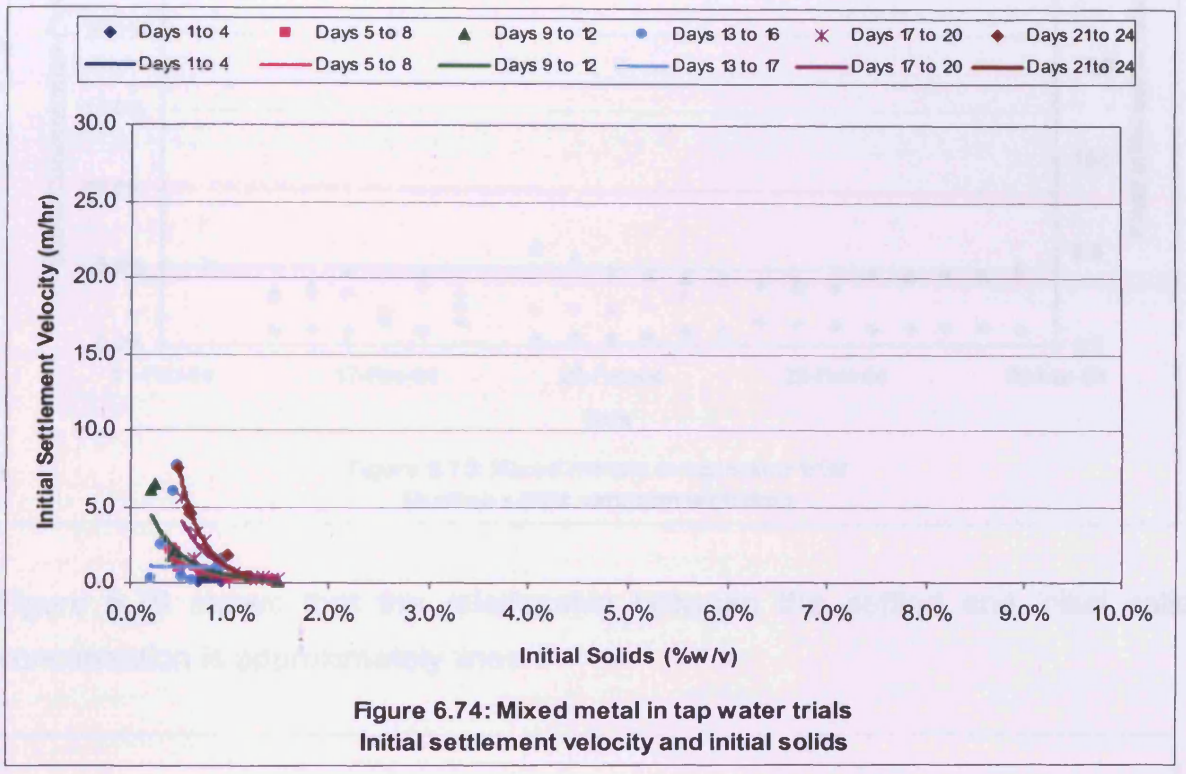


Figure 6.74: Mixed metal in tap water trials
Initial settlement velocity and initial solids

As previously shown, a general trend can be seen that as the sludge ages, the settlement velocity increases. However, the speed of the trends moving from left to right, in terms of days of plant operation, is slower than for any other trial. After 17 days of the trial, the initial solids was at 1% (w/v) and the settling velocity was only 1 m/hr. At the end of the trial, after a total of 24 days, the sludge settlement

6.9.12 Settled Solids Content

The variation in initial and settled mudline solids concentration after 2 hours is shown in Figure 6.75 and indicates a steady build up in the settled solids concentration throughout the duration of the trial. The data shows that by the end of the trial, the settled solids concentration had reached a peak value of 4.93% (w/v). Figure 6.75 also presents the ratio of final solids to initial solids and indicates an average of approximately 3.6 during the trial. The ratio was

approximately 3.1 on day 5, 3.2 on day 19 and by day 24 of the trial the ratio was 4.4.

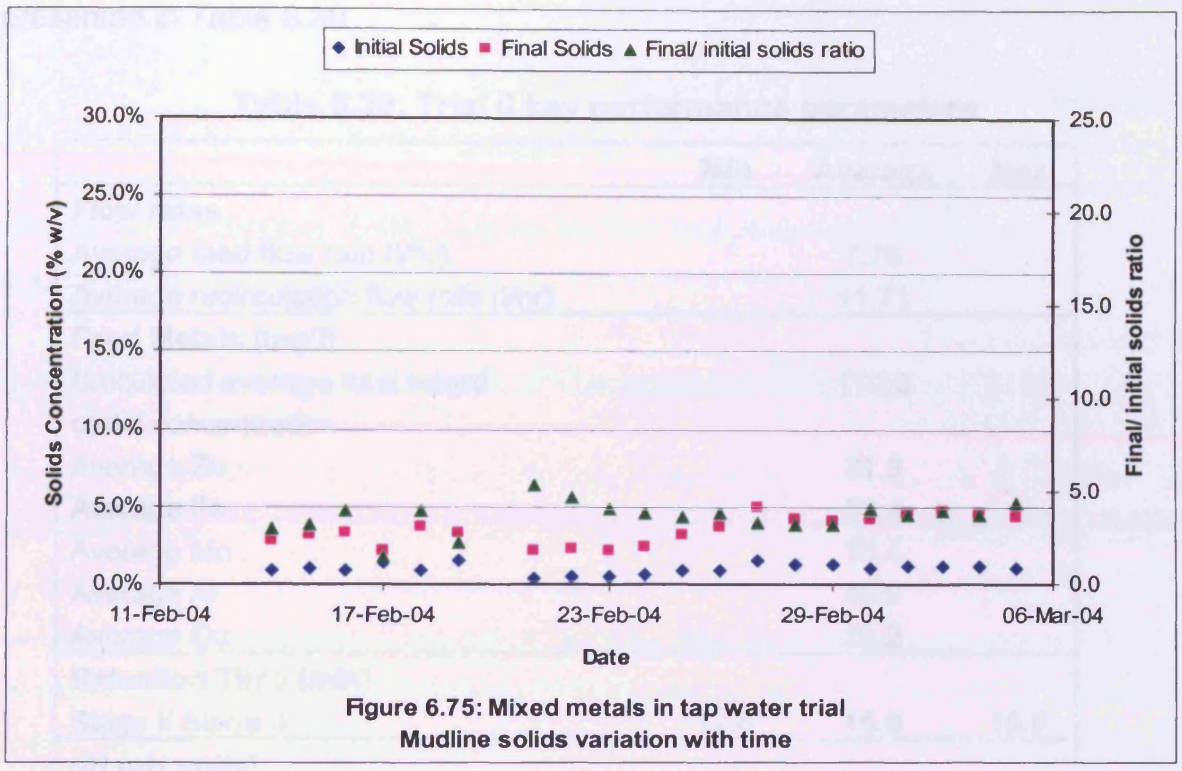


Figure 6.75: Mixed metals in tap water trial
Mudline solids variation with time

Figure 6.76 shows that the relationship between the settled and initial solids concentration is approximately linear.

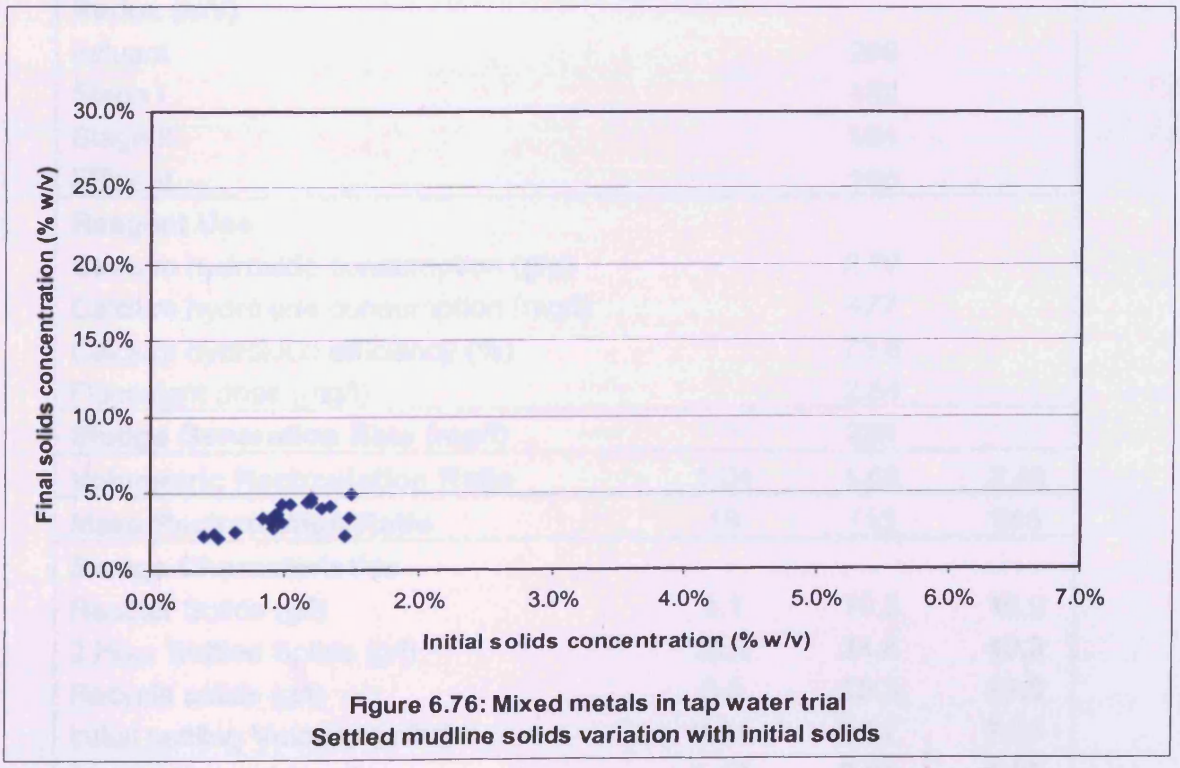


Figure 6.76: Mixed metals in tap water trial
Settled mudline solids variation with initial solids

6.9.13 Summary of Trial 6 Results

The key performance parameters of the mixed metals in tap water trial (Trial 6) are presented in Table 6.30.

Table 6.30: Trial 6 key performance parameters

	Min	Average	Max
Flow rates			
Average feed flow rate (l/hr)		7.75	
Average recirculation flow rate (l/hr)		11.71	
Feed Metals (mg/l)			
Calculated average total mixed metal concentration		172.3	
Average Zn		31.3	
Average Fe		51.4	
Average Mn		15.4	
Average Al		46.0	
Average Cu		28.2	
Retention Time (min)			
Stage I/ Stage II	12.8	15.6	19.8
pH (pH units)			
Influent	2.68	3.77	5.72
Stage I	4.54	7.06	8.77
Stage II	5.65	7.56	9.14
Effluent	5.54	7.48	9.17
Redox (mV)			
Influent		269	
Stage I		182	
Stage II		181	
Effluent		183	
Reagent Use			
Calcium hydroxide consumption (g/g)		2.77	
Calcium hydroxide consumption (mg/l)		477	
Calcium hydroxide efficiency (%)		73.6	
Flocculant dose (mg/l)		2.54	
Sludge Generation Rate (mg/l)		286	
Volumetric Recirculation Ratio	1.04	1.68	3.83
Mass Recirculation Ratio	19	113	345
Sludge Characteristics			
Reactor Solids (g/l)	4.1	10.2	15.0
2 Hour Settled Solids (g/l)	21.1	34.8	49.3
Recycle solids (g/l)	0.0	18.3	29.6
Initial settling Velocity (m/hr)	0.11	2.07	7.65
Final/ Initial solids ratio	1.48	3.62	5.27

Unlike previous trials the reactor solids did not reach a concentration of 4 % (w/v).

After day 17 the solids concentration was 1 % (w/v) and settled at approximately 1 m/hr.

During Trial 6, there appeared to be little relationship between the Stage I reactor pH and solids concentration (Figure 6.68).

On the 29th February 2004, day 19 of the trial, the final/initial flocculation tank solids ratio was approximately 3.2.

6.10 Discussion on Results of Continuous Pilot Plant Trials

Key to understanding if HDS sludge has been formed is to review the characteristics of the sludge generated (and most importantly the settling characteristics). This is undertaken by measuring the rate at which the sludge settles (the settlement velocity of the sludge), and how the volume occupied by the sludge after it has settled compared to the initial sludge volume (the ratio of settled solids with initial solids) changes with time. When looking at the data it is also important to consider the change in mass of solids in the sludge under review, as this will also affect the settlement characteristics.

6.10.1 Comparison of Sludge Settlement Velocities

Presented in Table 6.31 is a comparison of the settlement velocities of the sludges generated during each trial. To ensure that 'like with like' sludges are compared, the settlement velocities of sludge of the same age and same initial solids concentration have been calculated and ranked.

Table 6.31: Comparison of settlement velocities

Trial number	Trial name	Sludge age (days)	Initial solids concentration (% w/v)	Settlement velocity (m/hr)	Rank
1	Iron in tap water	17	4	8	2
2	Zinc in tap water	17	4	10	1
3	Aluminium in tap water	17	4	3	4
4	Manganese in tap water	17	4	8	2
5	Iron in seawater	17	4	2	5
6	Mixed metals in tap water	17	1	1	6

The sludge generated in Trial 2 (zinc in tap water) settled fastest, as the sludge of

4 % (w/v) had a settlement velocity of approximately 10 m/hr after 17 days. The effect of changing the Stage II reactor operating pH from 7.5 to 8.5 on the 18th November 2003 is unclear, however after the pH was increased, the settlement velocity (and ratio of settled/initial solids) increased. It is therefore considered that, if Trial 2 had started with an operating pH of 8.5, the settlement characteristics would have been improved.

Sludges generated in Trials 1 and 4 (iron in tap water and manganese in tap water) both achieved settlement velocities of 8 m/hr after 17 days, with an initial solids concentration of 4 % (w/v).

The settling velocities from Trials 3 and 4 (aluminium in tap water and iron in seawater) were 3 m/hr and 2 m/hr respectively. The sludges from these two trials therefore settled at less than a third (for aluminium in tap water) and a fifth (for iron in seawater) of Trial 2 (zinc in tap water).

The slowest settling sludge was the sludge generated in Trial 6 (mixed metals in tap water) which achieved a settling velocity of 1 m/hr. However, this was achieved with an initial solids concentration of 1 % (w/v), therefore if a sludge sample had been thickened to 4 % (w/v), the settlement velocity would have been extremely slow (see Figure 6.74).

The 4 day groupings of the settling velocities (Figures 6.15, 6.27, 6.39, 6.51, 6.62 and 6.74) can be used to indicate how quickly HDS sludge is formed during the trials. The groupings indicate that the formation of HDS sludge was fastest in Trials 2 (zinc in tap water) and 4 (manganese in tap water), whilst the formation of HDS sludge was slowest in Trial 6 (mixed metals).

The Wheal Jane HDS MWTP settling velocities were measured at 17 m/hr and 18 m/hr for Stream 1 and Stream 2 respectively. These settling rates are higher than those measured during the present research and are likely to of been as a result of the sludge having time to age and hence the HDS sludge had fully formed.

6.10.2 Comparison of Settled to Initial Solids Concentration Ratios

Presented in Table 6.32 is a comparison of the ratios of settled (post settlement test) sludge concentration to initial (pre settlement test) sludge concentration for the sludges generated during each of the trials. The settled to initial solids ratios for sludge of the same age (5 days and circa 19 days) have been calculated, as

has the average ratio for each trial. The average concentration has been used to rank the ratios. Due to different inlet metal concentrations and precipitation rates, the solids concentrations were not standardised. However, as the change in sludge concentration occupied was being reviewed, it was considered that comparing the ratios in Table 6.32 was acceptable.

The sludge generated in Trial 4 (manganese in tap water) produced an average ratio of settled to initial solids concentration of 10.9, the highest of all trials. During Trial 4, the ratio decreased from a ratio of 16.8 after day 5 of the trial to a ratio of 9.6 after 19 days of the trial. This indicates that the manganese hydroxide sludge has the capacity to form a very tightly compacted sludge.

Table 6.32: Comparison of settled to initial solids concentration ratios

Trial	Trial name	Start of trial settled /initial solids ratio		End of trial settled/initial solids ratio		Trial average final to initial solids ratio	Rank
		Ratio	Sludge age	Ratio	Sludge age		
1	Iron in tap water	5.4	5	5.4	16	4.2	3
2	Zinc in tap water	3.6	5	4.4	18	5.8	2
3	Aluminium in tap water	2.3	5	3.6	19	3.2	6
4	Manganese in tap water	16.8	5	9.6	19	10.9	1
5	Iron in seawater	4.8	5	2.6	19	3.9	4
6	Mixed metals in tap water	3.1	5	3.2	19	3.6	5

The average ratios for the sludges generated in the other 5 trials were 5.8 (Trial 2, zinc in tap water), 4.2 (Trial 3, iron in tap water), 3.9 (Trial 4, iron in seawater), 3.6 (Trial 6, mixed metals in tap water) and 3.2 (Trial 2, aluminium in tap water). These sludges occupied between approximately two and three times the volume occupied by the Trial 4 (manganese in tap water) sludge. Trial 3 (aluminium in tap water) sludge occupied 3.4 times the volume occupied by the Trial 4 (manganese in tap water) sludge and suggests that it was less tightly compacted and more voluminous.

The ratios of settled (post settlement test) sludge concentration to initial (pre settlement test) sludge concentration for the sludges generated at Wheal Jane HDS MWTP were 11.9 and 13.0 for Stream 1 and Stream 2 respectively. As with the settling velocities the improved performance is likely to of been as a result of the sludge having time to age and hence the HDS sludge had fully formed.

6.10.3 Comparison of Operating Parameters

In Table 6.31 and Table 6.32 the performance of each trial is presented according to the sludge settlement velocity and the ratios of settled (post settlement test) sludge concentrations to initial (pre settlement test) sludge concentrations. It has been proposed that the Stage I reactor pH (and hence zeta potential) (Dempsey *et al.* 1993) and the mass recirculation ratios (Kostenbader *et al.* (1970); Bosman (1974) are fundamental to the formation of HDS sludge. These parameters have been reviewed in Table 6.33 (Stage I reactor stable pH and solids concentration) and Table 6.32 (Mass recirculation and reactor solids/new solids ratios) below and compared with the Settlement velocities and the ability for the sludge to compact (i.e. ratio of settled to initial solids concentrations) and reduce its volume.

Presented in Table 6.33 is the comparison of the stabilised Stage I reactor pH and solids concentrations (i.e. the minimum solids concentration required to maintain a stable pH in the Stage I reactors).

Table 6.33: Comparison of Stage I stable pH and solids concentrations

Trial	Trial name	Days to stabilise (days)	Stable pH (pH units)	Reactor solids concentration (% w/v)	Rank
1	Iron in tap water	10	7.4	2.5	3
2	Zinc in tap water	12	8.5	1.5	1
3	Aluminium in tap water	12	6.8	4.0	5
4	Manganese in tap water	10	8.3	1.5	1
5	Iron in seawater	13	7.8	3.5	4
6	Mixed metals in tap water	17	8.5	Unclear	-

The trials have been ranked according to the solids concentration required to achieve a stable pH in the Stage I reactors (with the lowest solids concentration ranked first). Due to the reactor solids concentrations of Trials 2 and 4 (when both concentrations were 1.5 %w/v solids) being lower than those of the other trials it would be expected that a higher settlement velocity would be achieved due to reduced likelihood of hindered settlement occurring. Table 6.31 already shows that Trial 2 had the quickest settling sludge at a solids concentration of circa 4% w/v, if HDS sludge could be shown to of being formed at the reactor solids concentrations presented in Table 6.33 (and hence become the chosen Stage I reactor solids) the settlement velocity would be increased further.

The stabilisation of the Stage I reactor pH may be an indication that HDS sludge had been formed (or ideal HDS operating conditions have been met), hence all subsequent sludge formed is HDS sludge instead of voluminous conventional metal precipitation sludge. Therefore, for Trial 2 (zinc in tap water), a Stage I reactor solids concentration of only 1.5% (w/v) would be required for HDS sludge to be generated (see Section 6.5.4), hence a faster settlement rate than that presented in Table 6.31 would be expected due to less hindered settlement.

A description of the affect of Stage I Reactor pH on the precipitation process is given in Section 7.4 (Surface electro kinetic potential and point of zero charge).

Using the solids concentrations presented in Table 6.33, a ratio of reactor solids concentration to new solids can be calculated (i.e. g/l of old solids in the reactor per g/l of new solids). This ratio has been calculated for all six trials as an alternative operating parameter to the mass recirculation ratio and is presented in Table 6.34 (Trial 6 ratio may not be accurate as a stable Stage I reactor pH was not achieved).

Table 6.34: Comparison of mass recirculation and reactor solids/new solids ratios

Trial	Trial name	Reactor solids (% w/v)	Solids generation (g/l)	Mass recirculation ratio	Reactor solids/new solids ratio
1	Iron in tap water	2.5	0.407	99	61
2	Zinc in tap water	1.5	0.268	89	56
3	Aluminium in tap water	4.0	0.600	185	67
4	Manganese in tap water	1.5	0.370	87	41
5	Iron in seawater	3.5	0.707	89	50
6	*Mixed metals in tap water*	*1.0*	*0.285*	*87*	*35*

Note:
Trial 6 ratios may not be accurate as a Stable pH was not achieved.
Reactor solids/new solids ratio is calculated by dividing the reactor solids concentration by the new solids concentration.
Mass recirculation ratio is a ratio of Total recirculated solids in 1 hour to Total new solids produced in 1 hour.

The reactor solids concentration to new solids ratio indicates the minimum value required to maintain a stable pH in the Stage I reactor. During the trials the minimum requirement was 41 during Trial 4 (manganese in tap water), excluding Trial 6 results. Trial 3 (iron in seawater), with a ratio of 50, was the next lowest. The iron in tap water (Trial 1) ratio of 61 was slightly higher than the zinc in tap water (Trial 2) ratio of 56. The highest of all trials was the aluminium in tap water (Trial 3) at 67.

As a comparison, the mass recirculation ratios, the conventional way of controlling the solids concentration in HDS plants (see Section 2.8.2), required to achieve a stable Stage I reactor pH have also been calculated. By knowing the average minewater flow and new solids generation rate, the average recirculation rate and recirculation solids concentrations the recirculation solids concentrations can be calculated by dividing the recirculation solids load (g of recirculated solids per hour) by the solids generated from the minewater (g of new solids per hour) i.e. total recirculated solids to new total solids. These values are presented in Table 6.34. It is worth highlighting that the Mass Recirculation Ratios reported in the individual trial sections, e.g. Section 6.7.10 for Trail 4 (manganese in tap water), were reported as g of Total solids to g of new metal hydroxides, whilst the results presented in Table 6.34 are reported as g of Total recirculated solids to g of Total new solids.

Again, excluding Trial 6 (mixed metals in tap water), Trial 4 (manganese in tap water) produced the lowest required mass recirculation ratio of 87 followed by Trial 2 (zinc in tap water) at 89. The calculated mass recirculation ratio for Trial 5 (iron in seawater) was also 89, however due to the varying feed rate (see Section 6.8.4) during this trial, this figure is artificially low. The Trial 1 (iron in tap water) required mass recirculation ratio was 99, whilst a mass recirculation ratio of 185 was required to maintain a stable Stage I reactor pH during Trial 3 (aluminium in tap water).

6.10.4 Continuous Pilot Plant Conclusions

The continuous pilot plant trials were undertaken to confirm that HDS could be produced using; sodium hydroxide as the alkali reagent, feed water without iron present and to generate data to further investigate the characteristics of HDS sludge. The trials' four objectives, listed in Section 6.1, are discussed below.

Objective 1: Operate a laboratory pilot plant to generate Type II HDS sludge from various synthetic minewater using sodium hydroxide as the alkali reagent and note the difference in the sludge settlement characteristics.

The batch tests undertaken and reported in Chapter 5 showed that HDS sludge could be generated when using sodium hydroxide as the alkali reagent. These findings have been reproduced in the continuous pilot plant trials for a range of

synthetic minewater solutions (containing iron, zinc, manganese and aluminium) and treated with sodium hydroxide. Sludge settlement characteristics (settlement velocities and sludge volume reductions), similar to those achieved at the Wheal Jane MWTP (see Chapter 4), were measured. It is therefore concluded that as shown in Chapter 5 Type II HDS sludge can be produced on a range of synthetic minewater using sodium hydroxide as the alkali reagent and that calcium hydroxide is not required.

The sludge generated from Trial 2 (synthetic zinc minewater) produced the fastest settling sludge at 10 m/hr (compared to circa 18 m/hr at Wheal Jane MWTP) whilst the sludge generated during Trial 4 (synthetic manganese minewater) yielded the greatest reduction (approximately 11 times reduction) in sludge volume during settling (compared to circa 12 times reduction in volume at Wheal Jane MWTP).

The continuous trials also confirmed the results of the batch tests that non- or low iron bearing feed waters can produce HDS sludge and iron is not a requirement for the production of HDS sludge.

Objective 2: Show that HDS sludge can be generated from synthetic iron in seawater minewater using sodium hydroxide as the alkali reagent.

The results of the batch tests (Chapter 5) concluded that HDS sludge could not produced in less than 30 batch cycles from synthetic iron in seawater minewater. During Trial 5 (iron in sea water trial) sludge was generated with a settling velocity of 2 m/hr and the sludge volume reduced to approximately ¼ of its initial volume, hence Type II HDS sludge was produced from iron in seawater synthetic minewater. It was therefore shown that HDS sludge could be produced if the metals are in a saline (seawater) solution.

Objective 3: Examine the differences in behaviour between synthetic minewater containing bivalent and trivalent metals in solution.

Synthetic minewater solutions were generated using metals of varying valencies. Zinc, a bivalent metal, settled faster and to a smaller sludge volume than both aluminium and iron, trivalent, metals. It is therefore suggested that the valence of the metal removed does not affect the HDS process. It is also suggested that a valency change is not required to form HDS, i.e. changing iron from Fe (II) to Fe (III) as suggested by Kostenbader (1970) (see Section 2.8.1).

Objective 4: Generate Type II HDS sludge from different synthetic minewaters and examine the difference in the sludge settlement characteristics.

During the six continuous pilot plant trials, the sludge settling characteristics (settling velocity and reduction in sludge volume) were measured. The results of these measurements are presented in Table 6.31 (sludge settling velocity) and Table 6.32 (ratio of settled sludge concentrations to initial sludge concentrations hence reduction in sludge volume). The synthetic zinc minewater produced the sludge with the fastest settling velocity, whilst the synthetic manganese minewater produced the sludge with the highest settled to initial sludge ratio i.e. a greatest reduction in volume occupied after 2 hours of settlement.

Further analysis of the sludge properties were undertaken with the results presented in Chapter 7.

Additionally, the following can be summarised from the continuous pilot plant trials:

The synthetic manganese minewater required a reactor solids concentration to new solids concentration ratio of 41 (the lowest ratio of all trials) to produce a stable pH in the Stage I reactor. This equated to a mass recirculation ratio of 87 (g of recirculated sludge per g of new sludge produced).

The synthetic aluminium minewater required a reactor solids concentration to new solids concentration ratio of 67 (the highest value of all trials) to produce a stable pH in the Stage I reactor. This equated to a mass recirculation ratio of 185 (g of recirculated sludge per g of new sludge produced).

The present research has shown that each minewater has a unique reactor solids concentration to new solids concentration ratio (or mass recirculation ratio) and providing a minimum ratio is exceeded there is no additional benefit in running at higher ratios. This was also confirmed during the Wheal Jane MWTP operational data review which indicated if a mass recirculation ratio of 12.3 was exceeded no variation in the settling velocity was detected (see Section 4.5.12).

Finally, the present research has also shown that the rate of HDS formation is minewater specific, with the results from Trial 6 (mixed metals) indicating that the more complex the minewater mixture the slower the longer HDS sludge takes to form.

7 SLUDGE CHARACTERISTICS

7.1 Introduction

During the present research, high density sludge has been generated through simple laboratory batch tests and by continuous laboratory pilot plant trials. The laboratory batch test results were essentially mimicked during the continuous trials and showed that high density sludge could be generated in the absence of iron and by using sodium hydroxide rather than the traditional alkali reagent, calcium hydroxide.

To further develop an understanding of the mechanisms that contribute to the formation of high density sludge, a series of tests was undertaken to examine the sludge properties. The properties examined were: mineralogy (by X-Ray Diffraction, XRD), morphology (by Scanning Electron Microscopy, SEM, and Transmission Electron Microscopy, TEM), surface electrical potential (by measuring the zeta potential) and dewatering characteristics.

7.2 Experimental Procedures

The testing procedures outlined in Section 3.4 were undertaken on sludge samples generated within seven days of the start of each trial (termed 'young' sludge), and sludge samples taken from the pilot plant at the end of each trial (termed 'old' sludge). Additional tests were carried out on sludge produced by conventional precipitation (see Section 2.6) of iron in tap water by sodium hydroxide and calcium hydroxide. The synthetic minewater used for the production of the conventionally precipitated sludge was a synthetic minewater with an initial iron concentration of 200 mg/l of iron, with the iron added as Fe (II) chloride.

7.3 Results of X-ray Diffraction Analysis

It is reported in the literature (Demopoulos *et al.*, 1995; Dempsey *et al.*, 2003; Kuyuack *et al.*, 1993; Aubé et al, 1997) that the HDS process produces a crystalline sludge. By undertaking X-ray diffraction analysis the mineralogy of the solids generated were examined and the presence of any crystalline minerals detected. All X-ray diffraction analysis was undertaken by identical methodology (see Section 3.3.1) on the precipitates produced during the research to examine

its mineralogy. As discussed in Chapter 2, the sludge generated during active minewater treatment is often termed 'amorphous Fe (III) hydroxide' sludge. This amorphous sludge, often in the form of ferrihydrite (which does have some crystalline characteristics and can contain nano crystals (Jambor *et al.*, 1998) that are difficult to detect) can, under certain environmental conditions, transform to more stable crystalline minerals.

7.3.1 Continuous Trial 1 – Iron in Tap Water XRD Analysis Results

The X-ray diffractograms for precipitates generated during continuous Trial 1 (when sodium hydroxide was added to iron in tap water) are presented in Figure 7.1.

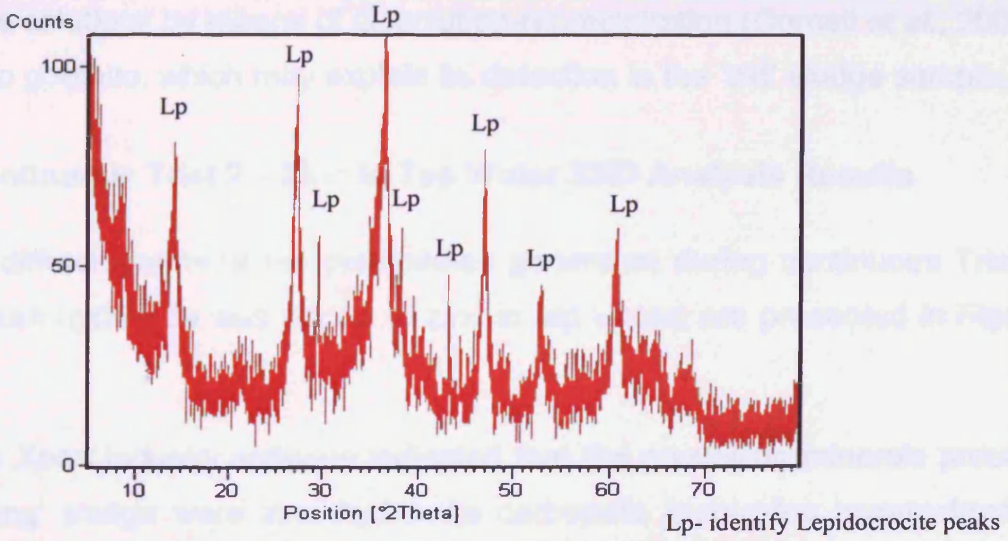


Figure 7.1a: Iron in tap water 'Young' sludge XRD

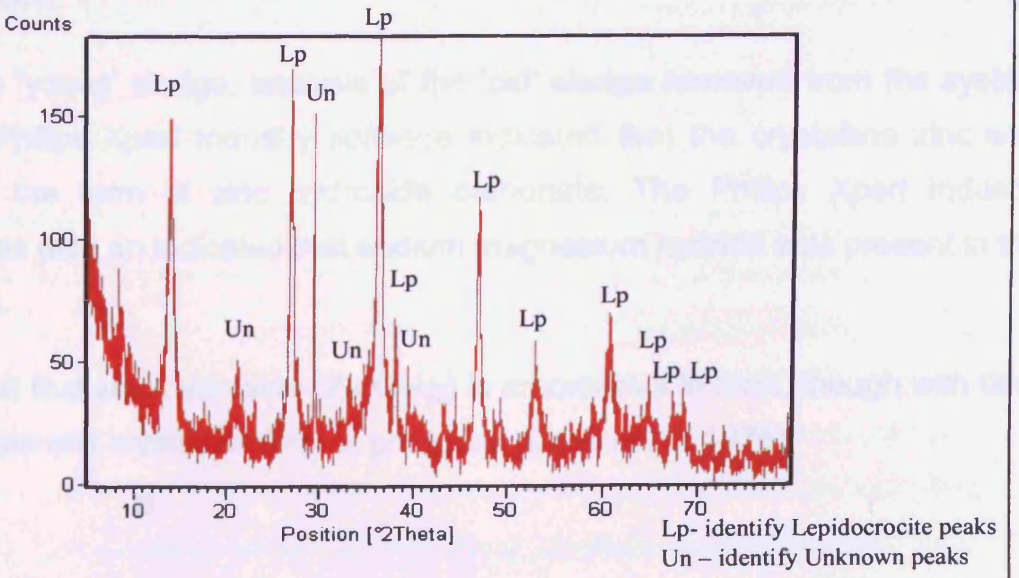


Figure 7.1b: Iron in tap water 'Old' sludge XRD

Figure 7.1: Iron in tap water 'young' and 'old' sludge XRD traces

Figure 7.1a shows the pattern for the 'young' sludge that was removed from the pilot plant on the 23rd September 05. The Philips Xpert Industry software indicated that the crystalline iron was present in the form of lepidocrocite (γ-FeO(OH)), lepidocrocite peaks are identified by label 'Lp' on Figure 7.1. As with the 'young' sludge, analysis of the 'old' sludge removed from the system on the 6th October 2003 using the Philips Xpert Industry software indicated that the crystalline iron was present in the form of lepidocrocite. There was also an indication that goethite (α-FeOOH) was present in the 'old' sludge, however this was a poor match. The height (counts) of the lines in Figure 7.1b are greater than those in Figure 7.1a, possibly indicating a more crystalline structure. Lepidocrocite (formed by oxidation of aqueous Fe (II) solutions) is scaly, fibrous or has massive aggregates (Bishop *et al.*, 1999) and is similar to goethite in chemistry. Lepidocrocite can (in acid Fe (II) sulphate solutions by means of dissolution-reprecipitation (Cornell *et al.*, 2003)) transform to goethite, which may explain its detection in the 'old' sludge sample.

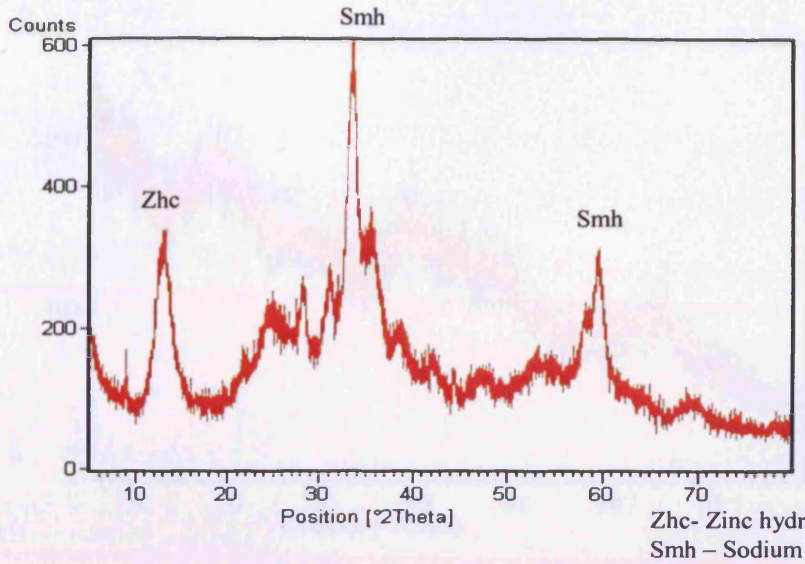
7.3.2 Continuous Trial 2 – Zinc in Tap Water XRD Analysis Results

The X-ray diffractograms of the precipitates generated during continuous Trial 2 (when sodium hydroxide was added to zinc in tap water) are presented in Figure 7.2.

The Philips Xpert Industry software indicated that the crystalline minerals present in the 'young' sludge were zinc hydroxide carbonate (pentazinc hexahydroxide carbonate) and sodium magnesium hydride, identified by Zhc and Smh on diffractograms.

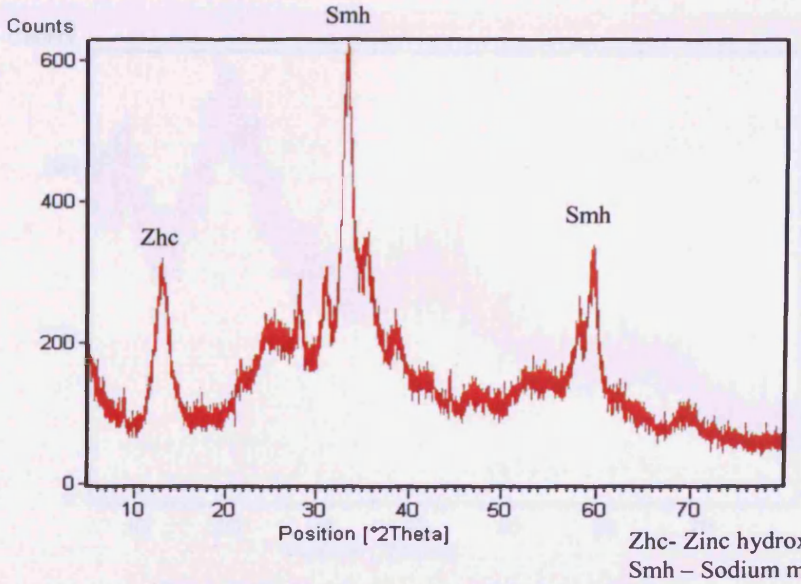
As with the 'young' sludge, analysis of the 'old' sludge removed from the system using the Philips Xpert Industry software indicated that the crystalline zinc was present in the form of zinc hydroxide carbonate. The Philips Xpert Industry software was also an indicated that sodium magnesium hydride was present in the 'old' sludge.

It is reported that zinc hydroxide ($Zn(OH)_2$) is amorphous in form, though with time a more stable and crystalline form is produced (Baes *et al.*, 1976).



Zhc- Zinc hydroxide carbonate
Smh – Sodium magnesium hydride

Figure 7.2a: Zinc in tap water 'Young' sludge XRD



Zhc- Zinc hydroxide carbonate
Smh – Sodium magnesium hydride

Figure 7.2b: Zinc in tap water 'Old' sludge XRD

Figure 7.2: Zinc in tap water 'young' and 'old' sludge XRD traces

7.3.3 Continuous Trial 3 – Aluminium in Tap Water XRD Analysis Results

The X-ray diffractograms of the precipitates generated during continuous Trial 3 (when sodium hydroxide was added to aluminium in tap water) are presented in Figure 7.3. No match to a mineral was found for the 'young', Figure 7.3a, or the 'old', Figure 7.3b, aluminium in tap water precipitates. The patterns indicate that there were no significant peaks, however the shape of the diffractograms would indicate that there was some crystalinity present. Boehmite (AlO(OH)) crystals are microscopic (nm in size, similar to the nano crystals in ferrihydrite), scattered grains and pea-like aggregates (Bishop *et al.*, 1999) and therefore, would not have been detected.

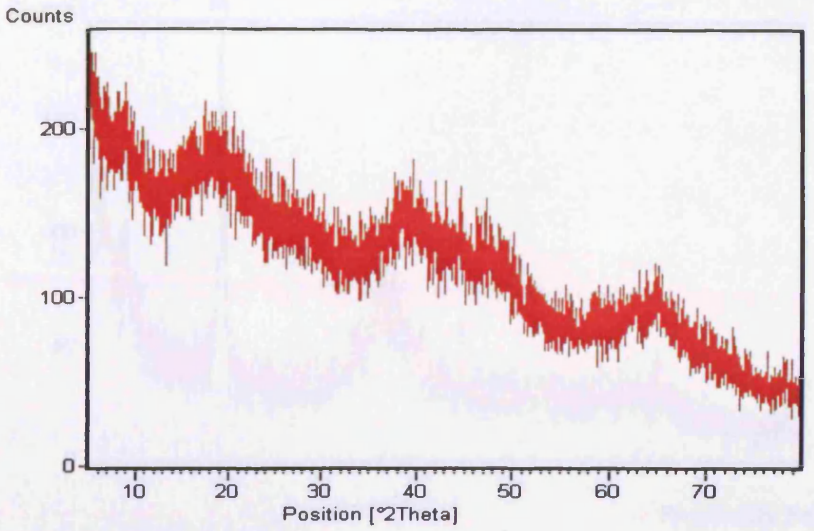


Figure 7.3a: Aluminium in tap water 'Young' sludge XRD

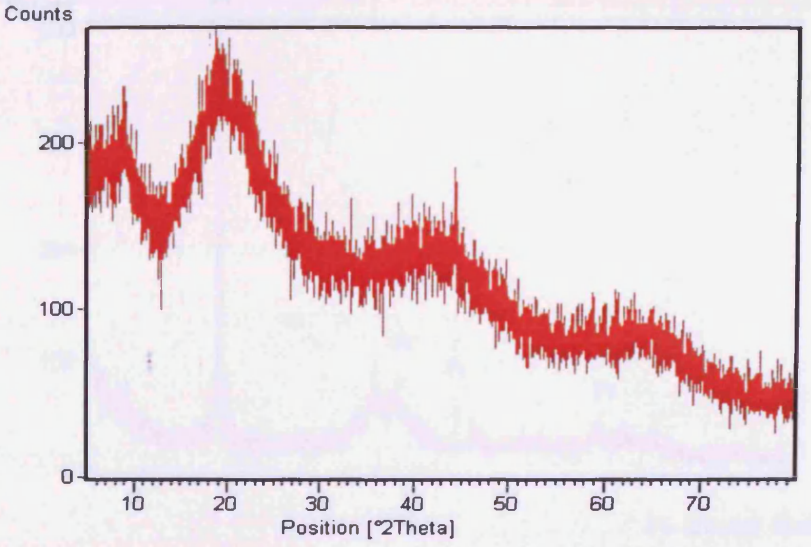


Figure 7.3b: Aluminium in tap water 'Old' sludge XRD

Figure 7.3: Aluminium in tap water 'young' and 'old' sludge XRD traces

7.3.4 Continuous Trial 4 – Manganese in Tap Water XRD Analysis Results

The software matched Feitknechtite (β-MnOOH, a manganese oxide hydroxide) to both the 'young' sludge, Figure 7.4a, and the 'old' sludge, Figure 7.4b, precipitates generated during Trial 4 (when sodium hydroxide was added to manganese in tap water). The height (counts) of the lines in Figure 7.4b 'old' sludge, are greater than those in Figure 7.4a 'young' sludge, possibly indicating a more crystalline structure. Feitknechtite eventually transforms to γ-MnOOH, manganite, with time (Watzlaf *et al.*, 1990).

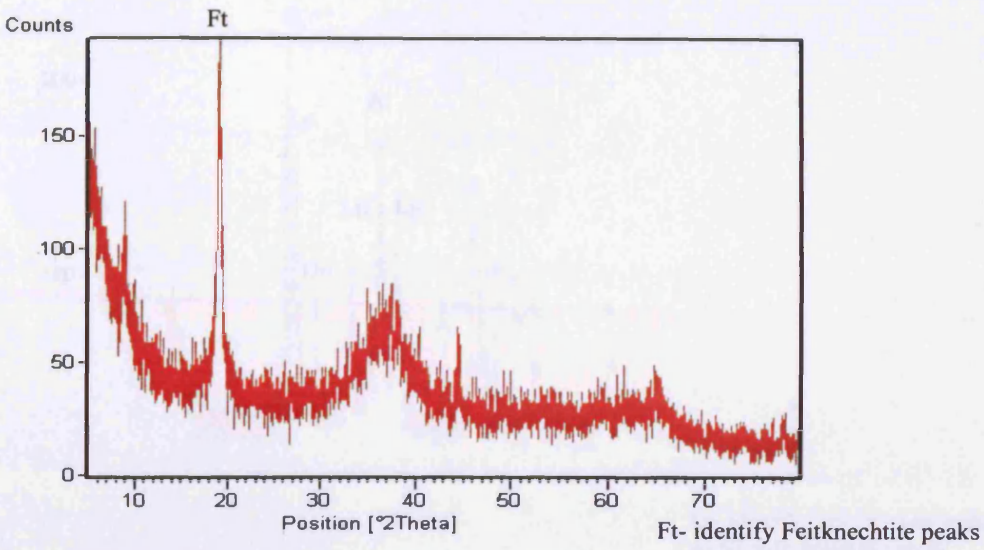


Figure 7.4a: Manganese in tap water 'Young' sludge XRD

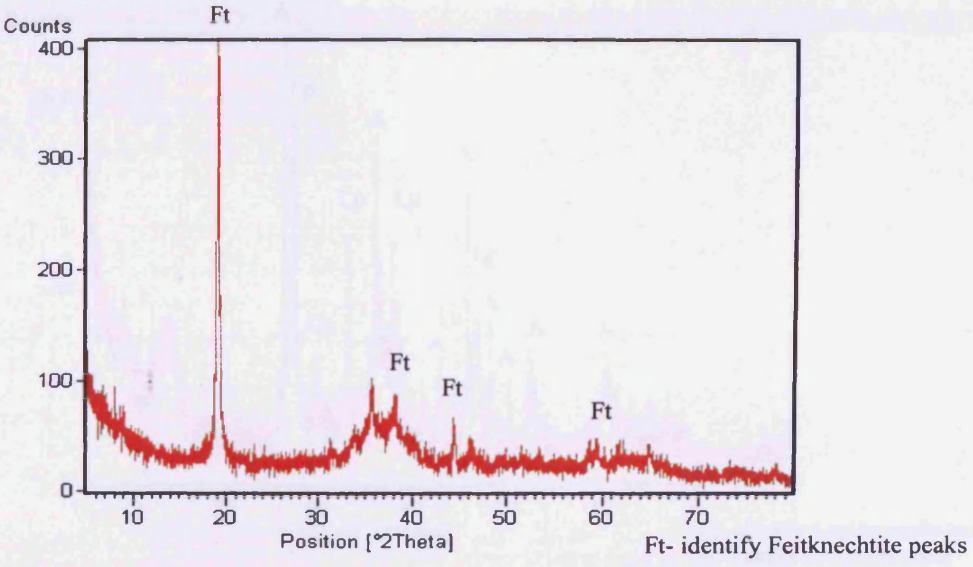


Figure 7.4b: Manganese in tap water 'Old' sludge XRD

Figure 7.4: Manganese in tap water 'young' and 'old' sludge XRD traces

7.3.5 Continuous Trial 5 – Iron in seawater XRD analysis results

Figure 7.5a shows the diffractograms for the 'young' sludge from Trial 5 (when sodium hydroxide was added to iron in seawater), with the crystalline iron mineral present identified as being lepidocrocite (γ-FeO(OH)). As with the 'young' sludge, the crystalline iron mineral in the 'old' sludge was lepidocrocite. There was also an indication that there was goethite (α-FeOOH) in the 'old' sludge, however this was a poor match. Both 'young' and 'old' sludge precipitates were found to contain aragonite ($CaCO_3$), likely to be present due to the added calcium in the seawater.

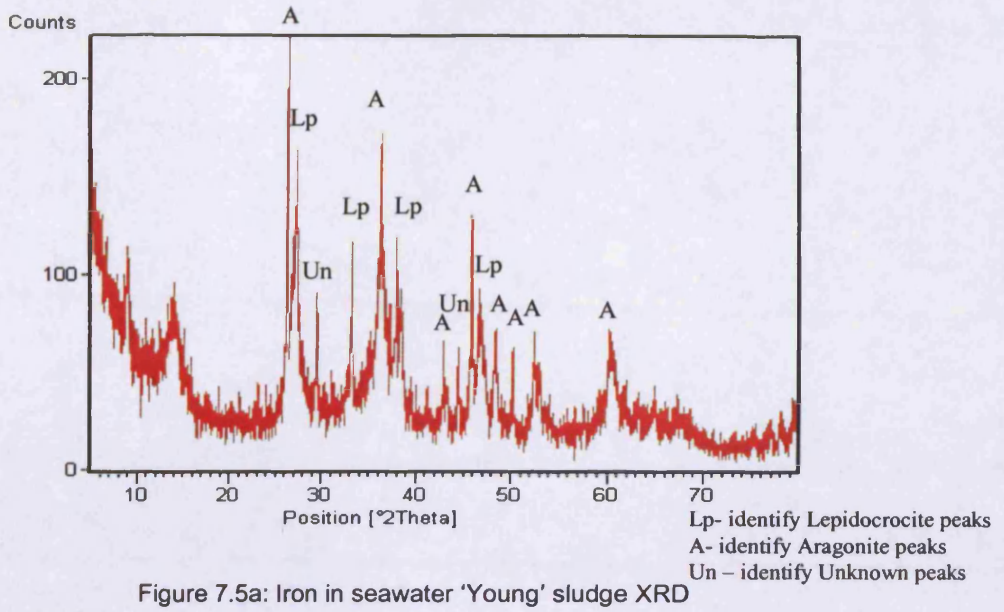


Figure 7.5a: Iron in seawater 'Young' sludge XRD

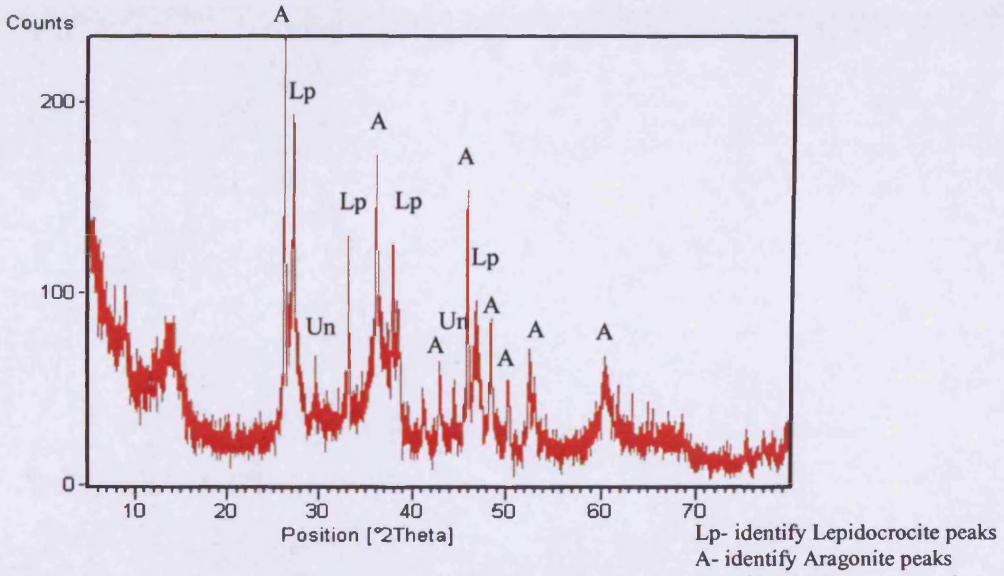


Figure 7.5b: Iron in seawater 'Old' sludge XRD

Figure 7.5: Iron in seawater 'young' and 'old' sludge XRD traces

7.3.6 Continuous Trial 6 – Mixed Metals in Tap Water XRD Analysis Results

As with the diffractograms for Trials 3, the Philips Xpert Industry software indicated no match to a mineral for the 'young' sludge, Figure 7.6a, precipitates from Trial 6 (when calcium hydroxide was added to mixed metal solution in tap water). However calcite (calcium carbonate) was detected in the 'old' sludge precipitates, Figure 7.6b.

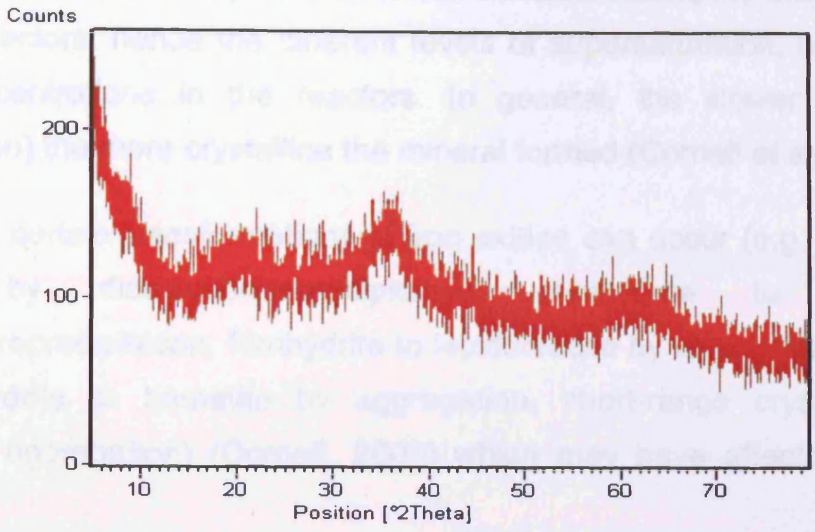


Figure 7.6a: Mixed metals in tap water 'Young' sludge XRD

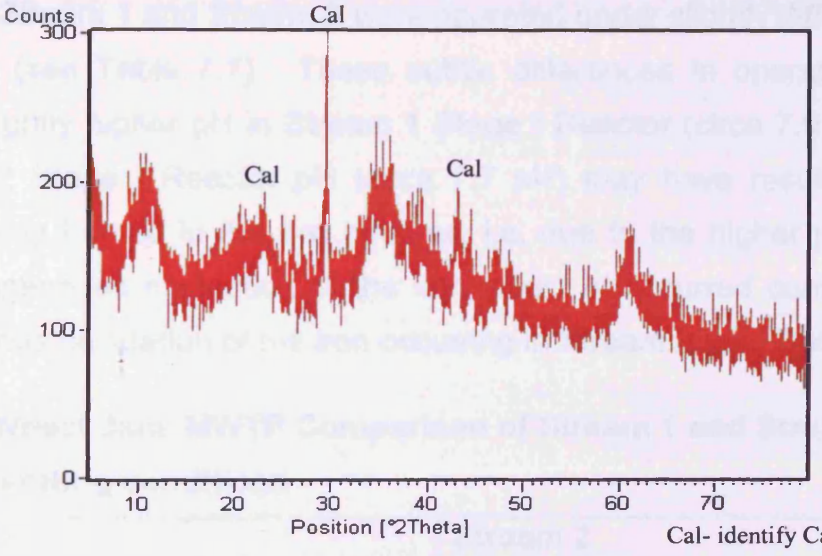


Figure 7.6b: Mixed metals in tap water 'Old' sludge XRD

Figure 7.6: Mixed metals in tap water 'young' and 'old' sludge XRD traces

7.3.7 Comparison of Pilot Plant and Wheal Jane XRD Analysis Results

Due to calcium hydroxide being used as the alkali reagent at the Wheal Jane MWTP calcite was detected in the Wheal Jane precipitates analysed by XRD diffraction (see Figure 4.35 Section 4.5.18). No crystalline iron minerals were detected in the Wheal Jane MWTP precipitates by the XRD Philips software.

However, during the continuous pilot plant trials which had iron in the minewater (i.e. Trials 1 and 5) lepidocrocite and goethite were detected in the sludge precipitates.

The different minerals formed in the two systems were possibly due to a

combination of the different minewater iron concentrations, the different pHs in the Stage I Reactors, hence the different levels of supersaturation, and the different solids concentrations in the reactors. In general, the slower the hydrolysis, (precipitation) the more crystalline the mineral formed (Cornell *et al.*, 2003).

In addition, certain transformations in iron oxides can occur (e.g. lepidocrocite to goethite by dissolution/reprecipitation, ferrihydrite to goethite by dissolution/reprecipitation, ferrihydrite to lepidocrocite by dissolution/reprecipitation and ferrihydrite to hematite by aggregation, short-range crystallazation with ferrihydrite aggregation) (Cornell, 2003) which may have affected the minerals formed.

It is also worth noting that at Wheal Jane MWTP due to the chosen set up conditions, Stream 1 and Stream 2 were operated under slightly different operating parameters (see Table 7.1). These subtle differences in operating conditions, including slightly higher pH in Stream 1 Stage I Reactor (circa 7.9 pH) compared to Stream 2 Stage I Reactor pH (circa 7.7 pH) may have resulted in different minerals being formed in the two streams, i.e. due to the higher pH in Stream 1 more homogeneous nucleation of the iron would of occurred compared to more heterogeneous nucleation of the iron occurring in Stream 2 (see Section 2.11).

Table 7.1: Wheal Jane MWTP Comparison of Stream 1 and Stream 2 Stage I Reactor operating conditions

Stream 1	Stream 2
Sludge colour: dark reddish brown	Sludge colour: brown-reddish yellow
Solids concentration ~3% w/v	Solids concentration ~2% w/v solids
61 min retention time	75 min retention time
Stage 1 average pH 7.9	Stage 1 average pH 7.7
(range 7.4 to 8.8)	(range 7.3 to 8.3)
More homogeneous nucleation	More heterogeneous nucleation
Possible mineral - Ferrihydrite	Possible mineral – Lepidocrocite or Goethite

This could possibly explain the different colours (shown in Figure 4.11) of the sludge in the two process streams, as ferrihydrite is a much darker brown colour compared to the more reddish colour of lepidocrocite (see Table 7.2 where the colour variations of iron oxide minerals are summarised).

Table 7.2: Colours of various iron oxide minerals (Schwertmann *et al.*, 2000)

Iron oxide mineral	Colour
Hematite	Red
Maghemite	Red to Brown
Magnetite	Black
Goethite	Brownish-reddish yellow
Lepidcrocite	Reddish yellow
Akaganetite	Brownish yellow
Ferrihydrite	Dark reddish brown
Feroxyhyte	Dark reddish brown
Schwertmannite	Reddish yellow

7.3.8 Comparison with Conventionally Precipitated 'Single Pass' Sludge

The X-ray diffraction diffractograms of the conventionally precipitated sludge generated, when calcium hydroxide and sodium hydroxide were used as the alkali reagent, are presented in Figure 7.7. The synthetic minewater used for the production of these precipitates was a synthetic iron minewater, with an initial iron concentration of 200 mg/l of iron with the iron added as Fe (II) chloride.

Figure 7.7a shows the diffractogram for the precipitates generated when calcium hydroxide was used as the alkali reagent. The Philips Xpert Industry software indicated that the only mineral present was calcite ($CaCO_3$), identified by Cal in Figure 7.7a. No crystalline iron minerals were detected.

The Philips Xpert Industry software indicated could not identify the peak detected, Figure 7.7b, in the precipitates generated when sodium hydroxide was used as the alkali reagent. However, the presence of the unidentified peak indicates that there was some crystalline mineral present. As the sodium hydroxide precipitation occurred very rapidly in a single reaction vessel, the formation of ferrihydrite might have been expected.

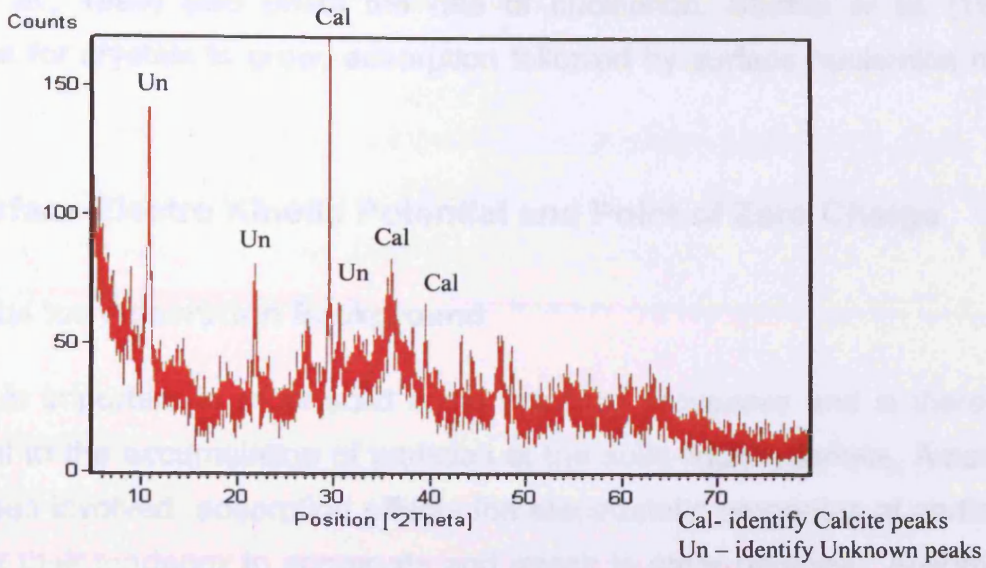


Figure 7.7a: Single pass $Ca(OH)_2$ sludge XRD

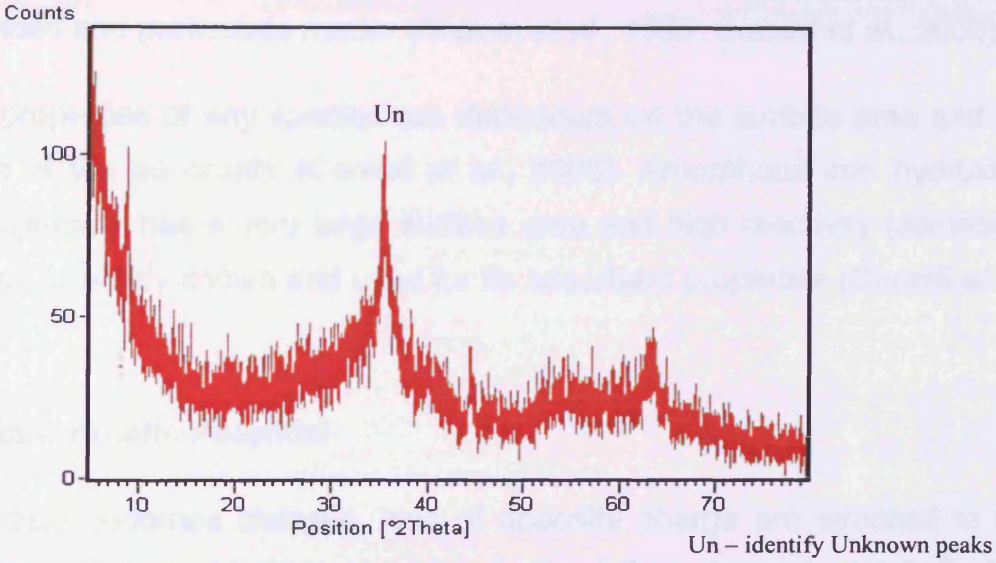


Figure 7.7b: Single pass NaOH sludge XRD

Figure 7.7: Single pass sludge XRD traces

7.3.9 X-Ray Diffraction – Summary

The X-ray diffraction analysis indicates that the rate of hydrolysis is important in the formation of crystalline minerals, however a more detailed examination is required to confirm this. By controlling the rate of oxidation and the operating pH, the mineral generated is affected (Cornell *et al.*, 2003). By slowing the process down, a more crystalline mineral is usually formed due to the rate of precipitation that is allowed to occur, i.e. heterogeneous nucleation can occur (Stumm *et al.*, 1996; Dempsey *et al.*, 2003). Whilst allowing the process to occur instantaneously, sludge of a more amorphous appearance is generated. Environmental conditions such as level of saturation, interfacial energy, collision frequency and temperature

(Stumm *et al.*, 1996) also affect the rate of nucleation. Stumm *et al.* (1996) suggest that for crystals to grow, adsorption followed by surface nucleation must first occur.

7.4 Surface Electro Kinetic Potential and Point of Zero Charge

7.4.1 Metal Ion Adsorption Background

Adsorption is important in most solid liquid interface processes and is therefore fundamental to the accumulation of particles at the solid-liquid interface. Amongst the processes involved, adsorption affects the electrostatic properties of particles, which affect their tendency to aggregate and attach to other particles. Adsorption also affects the reactivity of surfaces and the distribution of substances between the liquid phase and particulate matter (Stumm *et al.*, 1996; Cornell *et al.*, 2003).

Adsorption properties of any species are dependent on the surface area and the particle size of the adsorbate (Cornell *et al.*, 2003). Amorphous iron hydroxide, ferrihydrite, typically has a very large surface area and high reactivity (Jambor *et al.*, 1998) and is widely known and used for its adsorbent properties (Cornell *et al.*, 2003).

7.4.2 Electro Kinetic Potential

When a particle becomes charged, ions of opposite charge are attached to the surface of the particle and held in place by electrostatic and van der Walls forces, which are strong enough to overcome thermal agitation. A diffuse layer of ions is formed around this fixed layer of ions, however, the forces are not great enough to form a compact double layer due to thermal agitation. The zeta potential is essentially the potential drop across the diffuse part of the double layer (Stumm *et al.*, 1996; Hiemenz *et al.*, 1997).

The surface charge of particles is dependent on the composition of the particle, size and shape of the particle and upon the nature of the chemical environment and in particular the pH. The attraction of anions and cations to iron hydroxides is pH dependent (Kosmulski *et al.*, 2003), due to the effect of pH on surface charge. At a low pH, iron hydroxides typically have a positive potential and at a high pH the potential is negative, i.e. the further away from the point of zero charge (PZC) the pH becomes, the more negative, or positive, the potential can become, hence at a

certain pH the charge can become zero (the point of zero charge (PZC)). This is true not only for iron hydroxides but for all metal hydroxides.

Much work has been undertaken on the PZC of various pristine minerals, with reviews and collation undertaken by Kosmulski (2003) and Parks (1964). Table 7.3 summaries the reported PZC for various pristine minerals, including iron oxides and hydroxides; aluminium oxides and hydroxides; manganese hydroxides and zinc oxides.

Table 7.3: Summary of cited pristine PZCs (Parks, 1964; Kosmulski, 2004; Kosmulski *et al.*, 2003)

Mineral		Range of PZC	Average PZC
Iron oxy hydroxides	Goethite (i)	3.2 – 7.2	5.9
	Goethite (ii)	6.7 – 9.2	8.5
	Goethite (iii)	-	8.3
	Goethite (iv)	7.5 – 9.5	8.8
	Lepidocrocite (i)	5.3 – 7.4	6.5
	Lepidocrocite (iv)	6.7 – 7.5	7.1
	Amorphous Hydroxides (i)	4.3 – 8.5	7.2
	Ferrihydrite (iv)	7.8 – 7.9	7.9
	FeOOH mixtures (iii)	-	7.3
	Fe (III) hydroxides (iii)	-	8.0
Aluminium oxy hydroxides	Boehmite (i)	6.5 – 9.4	8.0
	Diaspore (i)	5.4 – 7.5	6.5
	Gibbsite (i)	3.8 – 5.2	5.4
	Gibbsite (ii)	9.0	9.0
	Bayerite (i)	5.4 – 9.3	7.9
	AlOOH (ii)	8.5 – 9.0	8.8
Manganese hydroxide	$Mn(OH)_2$ (i)	7.0	7.0
	Manganite (ii)	5.4	5.4
Zinc oxide	ZnO (i)	8.7 – 10.3	9.3
	ZnO (i)	7.5 – 9.6	8.8

Range of PZC is the range of all cited data collated by reference
Average PZC is the average of the cited data collated by reference
(i) Parks, 1964
(ii) Kosmulski, 2004
(iii) Kosmulski *et al.*, 2003
(iv) Cornell *et al.*, 2003

Work undertaken by Dempsey (1993) indicated that a 4-fold increase in the sludge density could be produced by the manipulation of the pH and the zeta potential of the sludge whilst Bosman (1970) identified the electro kinetic potential as an important factor in the formation of HDS sludge. Electro kinetic potential measurements were therefore undertaken on the sludge generated during the

continuous pilot plant trials.

7.4.3 Microelectrophoresis Results

The electrokinetic potential (or Zeta potential) was measured in the pH corrected 'young' and 'old' sludge samples taken from continuous pilot plant Trials 1 to 5, as described in Section 3.5.2.

The pH of the samples was also measured, enabling the zeta potential to be plotted against pH, thus yielding the point of zero charge for each of the sludges produced.

7.4.4 Continuous Trial 1 (Iron in Tap Water) Zeta Potential Measurements

The results of the zeta potential measurements for the Continuous Trial 1 (iron in tap water) are presented in Figure 7.8.

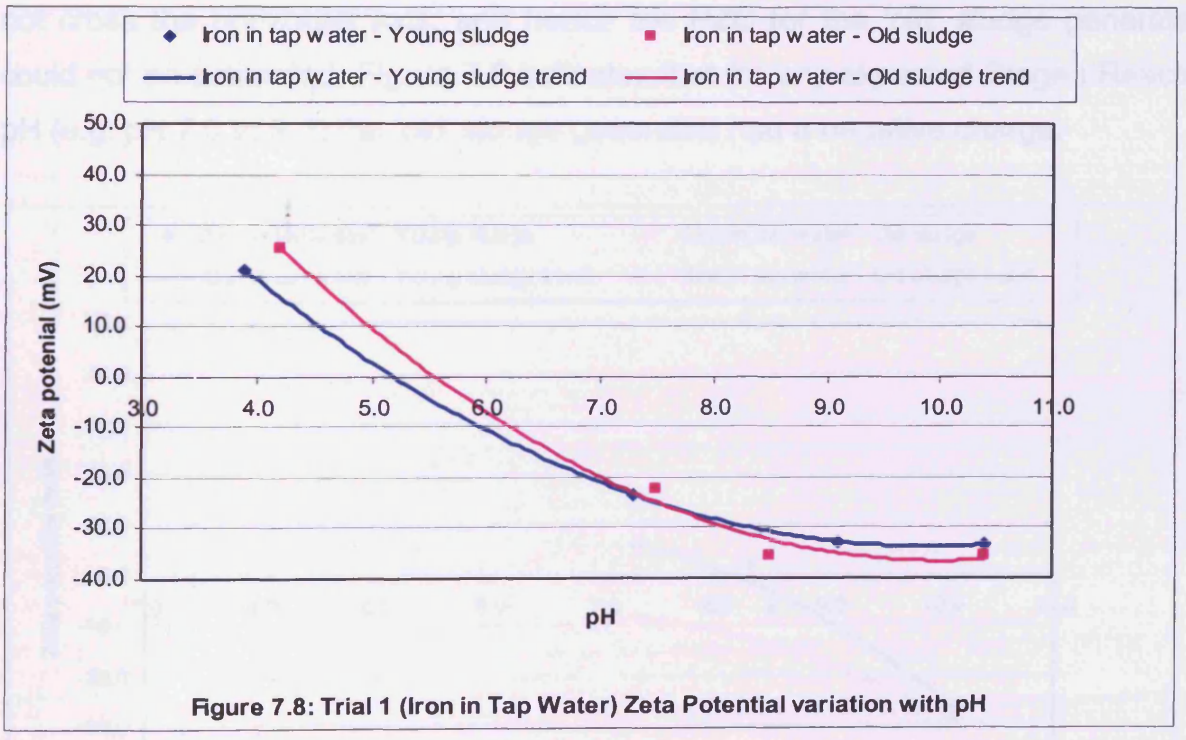


Figure 7.8: Trial 1 (Iron in Tap Water) Zeta Potential variation with pH

Figure 7.8 showed that, as the sludge aged (from 5 days to 18 days), the PZC of the solids produced increased from a pH of approximately 5.2 to a pH of 5.6. This is lower than the reported average PZC values for pristine iron hydroxides presented in Table 7.3, though does fall in the range cited by Parks (1964) for lepidocrocite. The results indicate that, as long as the pH of the solution remained above 5.6, the iron hydroxide solids produced during Trial 1 would remain

negatively charged.

During the initial stages of the trial, when the Stage I Reactor pH was 6.1, the zeta potential was -12 mV. The pH in the Stage I Reactor in Trial I stabilised at 7.4, this gave a zeta potential of approximately -24 mV. This indicated that, as the trial proceeded and the Stage I Reactor operating pH increased, the zeta potential of the sludge in the Stage I Reactor became more negative. Therefore, the sludge became more attractive to the fresh metal cations in the minewater, Section 7.4.2.

7.4.5 Continuous Trial 2 (Zinc in Tap Water) Zeta Potential Measurements

The PZC for the start of Trial 2 (zinc in tap water) sludge was at a pH of 8.1, Figure 7.9, as with the Trial 1, this PZC is lower than the cited average PZCs presented in Table 7.3. As the trial proceeded, the zeta potential of the sludge in the Stage 1 Reactor (operating pH range 8.1 to 8.5) became more negative. The trend line through the measured zeta potential readings of the 'old' sludge does not cross the horizontal axis, and hence the PZC for the 'old' sludge generated could not be estimated. Figure 7.9 indicates that for any expected Stage I Reactor pH (e.g. pH 7.0 to 9.5) the 'old' sludge generated had a negative charge.

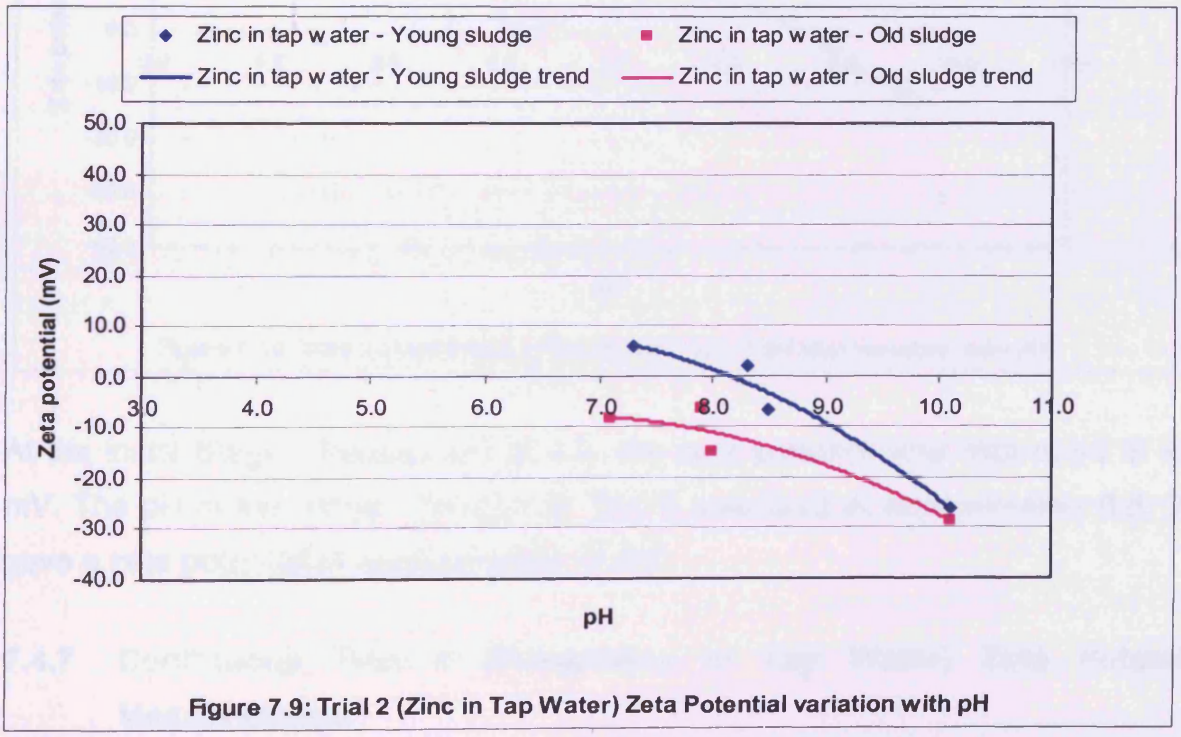


Figure 7.9: Trial 2 (Zinc in Tap Water) Zeta Potential variation with pH

At the initial Stage I Reactor pH of 7.5, the zeta potential was measured at +5 mV. The pH in the Stage I Reactor increased during Trial 2 and stabilised at 8.5, giving a zeta potential of approximately -14 mV. The sample of 'young' sludge was taken

on the 15th November 2003, three days before the Stage II reactor pH was changed from 7.5 to 8.5, and when there were problems with the sludge settleability.

7.4.6 Continuous Trial 3 (Aluminium in Tap Water) Zeta Potential Measurements

Figure 7.10 presents the zeta potential measurements for the Trial 3 (aluminium in tap water), and shows that, as the trial proceeded and the sludge aged (from 4 days old to 19 days old), the PZC of the solids generated decreased from a pH of approximately 8.6 to a pH of 6.6. This is within the PZC range of Boehmite reported by Parks (1964).

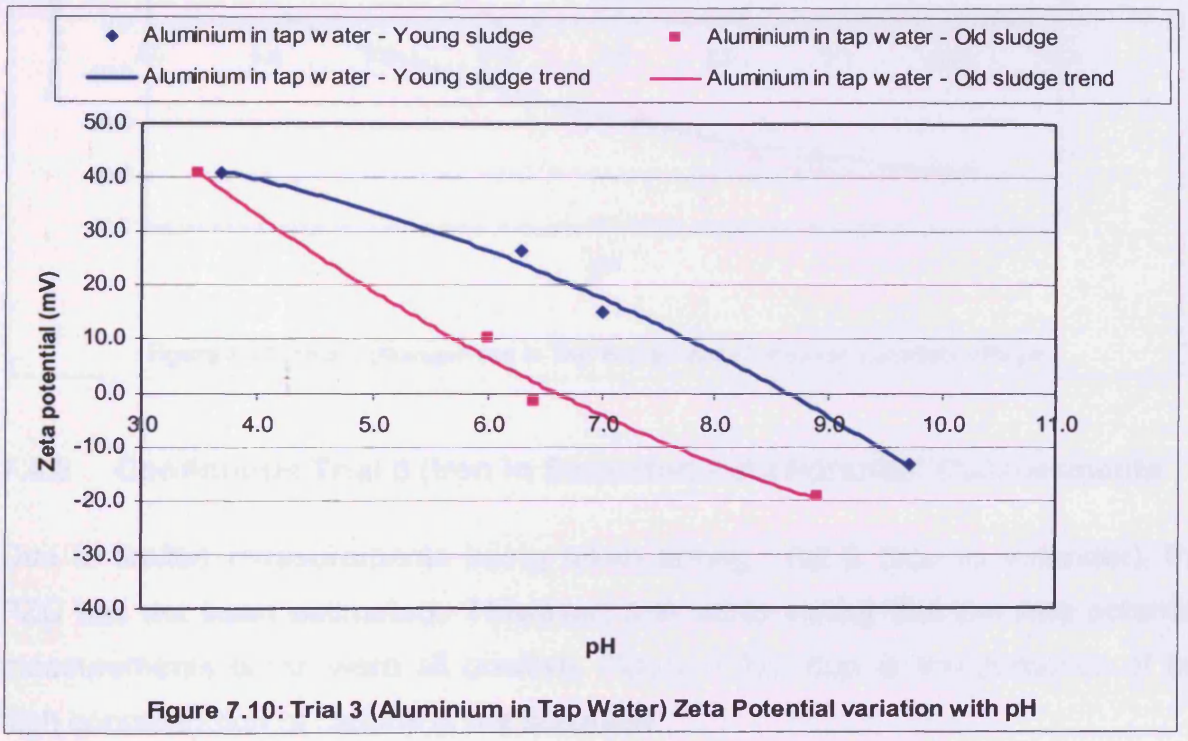


Figure 7.10: Trial 3 (Aluminium in Tap Water) Zeta Potential variation with pH

At the initial Stage I Reactor pH of 4.5, the zeta potential was measured at +37 mV. The pH in the Stage I Reactor in Trial 3 stabilised at approximately 6.8; this gave a zeta potential of approximately -2 mV.

7.4.7 Continuous Trial 4 (Manganese in Tap Water) Zeta Potential Measurements

As the sludge aged during Trial 4 (manganese in tap water), from 7 days old to 21 days old, the PZC of the solids generated increased from a pH of approximately 4.4 to a pH of 6.1, Figure 7.11.

At the initial Stage I Reactor pH of approximately 8.0, the zeta potential was measured at -22 mV. The pH in the Stage I Reactor in Trial 4 stabilised at approximately 8.3; this gave a zeta potential of approximately -26 mV, which was narrowly the lowest value of all the trials (Trial 1 'old' sludge gave a zeta potential of -24 mV).

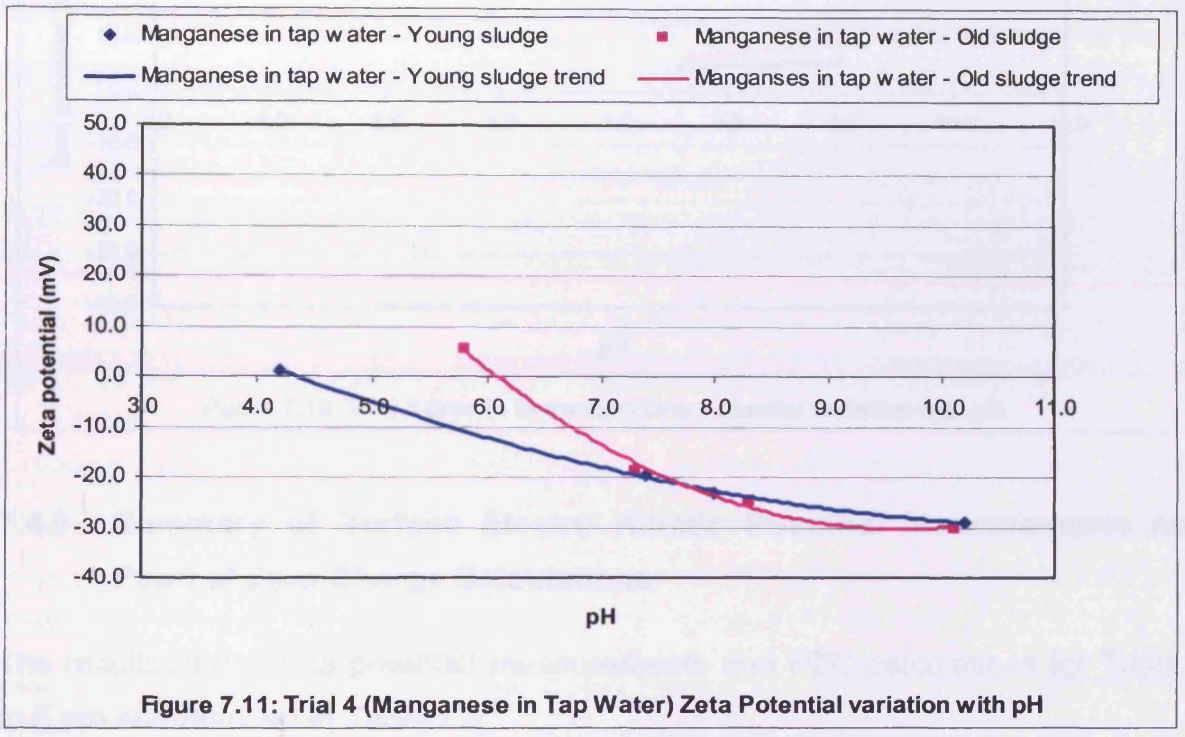


Figure 7.11: Trial 4 (Manganese in Tap Water) Zeta Potential variation with pH

7.4.8 Continuous Trial 5 (Iron in Seawater) Zeta Potential Measurements

Due to limited measurements being taken during Trial 5 (iron in seawater), the PZC has not been estimated. However, it is worth noting that the zeta potential measurements taken were all positive, Figure 7.12., due to the presence of the high concentration of cations in the seawater.

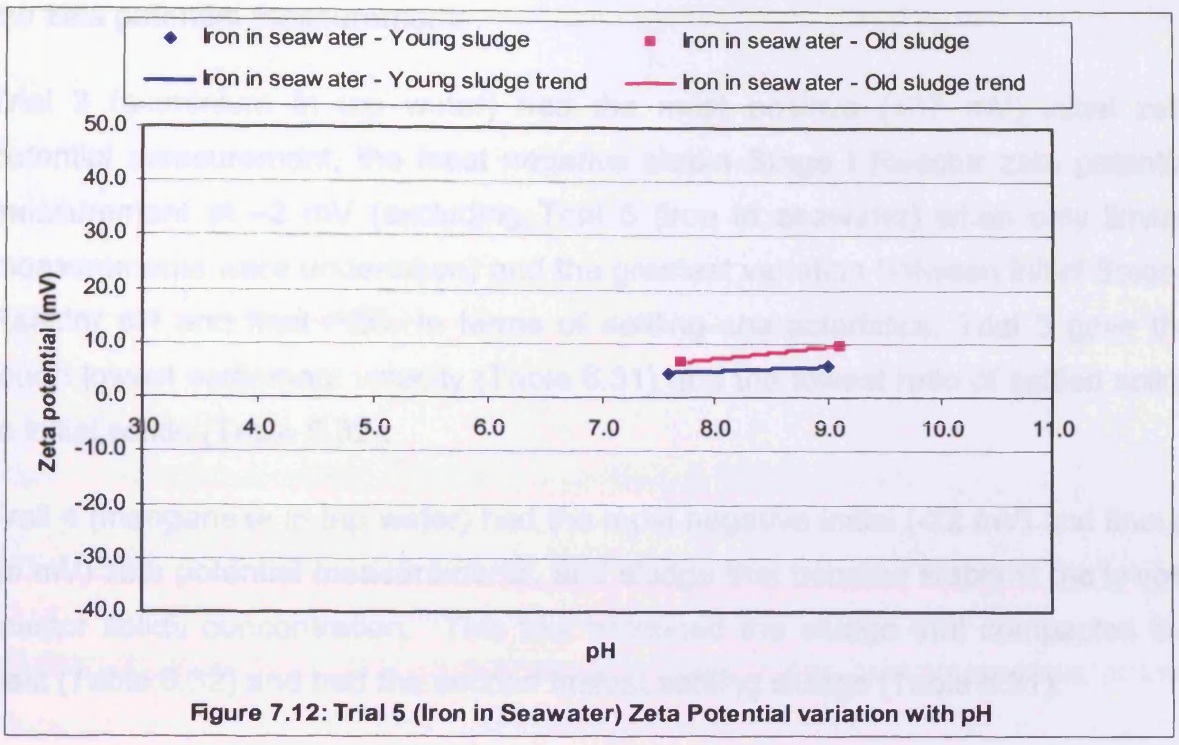


Figure 7.12: Trial 5 (Iron in Seawater) Zeta Potential variation with pH

7.4.9 Summary of Surface Electro Kinetic Potential Measurements and Point of Zero Charge Calculations

The results of the zeta potential measurements and PZC calculations for Trials 1 to 5 are summarised in Table 7.4.

Table 7.4: Comparison of zeta potential and point of zero charge for sludges from Trials 1 to 5

Trial Number	Sample Date	Sludge Age (days)	PZC (pH_0)	Initial Stage I pH	Zeta potential at initial pH (mV)	Stable Stage I pH	Zeta potential at stable pH (mV)
Trial 1 - Iron in tap water	23 Sept 03	5	5.2	6.1	-12	-	-
Trial 1 - Iron in tap water	06 Oct 03	1	5.6	-	-	7.4	-24
Trial 2 - Zinc in tap water	15 Nov 03	6	8.1	7.5	+5	-	-
Trial 2 - Zinc in tap water	27 Nov 03	18	-	-	-	8.5	-14
Trial 3 - Aluminium in tap water	04 Dec 03	4	8.6	4.5	+ 37	-	-
Trial 3 - Aluminium in tap water	19 Dec 03	19	6.6	-	-	6.8	-2
Trial 4 - Manganese in tap water	16 Mar 04	7	4.4	8	-22	-	-
Trial 4 - Manganese in tap water	30 Mar 04	21	6.1	-	-	8.3	-26
Trial 5 – Iron in seawater	12 Oct 03	6	-	7.5	+ 4	-	-
Trial 5 – Iron in seawater	30 Oct 03	24	-	-	-	7.8	+ 7

The results indicate that the chosen operating pH (and hence the stable Stage I Reactor pH) and the age of the sludge (in terms of days from start of trial) affect

the zeta potential measurements.

Trial 3 (aluminium in tap water) had the most positive (+37 mV) initial zeta potential measurement, the least negative stable Stage I Reactor zeta potential measurement at –2 mV (excluding Trial 5 (iron in seawater) when only limited measurements were undertaken) and the greatest variation between initial Stage I Reactor pH and final PZC. In terms of settling characteristics, Trial 3 gave the fourth lowest settlement velocity (Table 6.31) and the lowest ratio of settled solids to initial solids (Table 6.32).

Trail 4 (manganese in tap water) had the most negative initial (-22 mV) and final (-26 mV) zeta potential measurements, and sludge that became stable at the lowest reactor solids concentration. This trial produced the sludge that compacted the best (Table 6.32) and had the second fastest settling sludge (Table 6.31).

Considering the results of Trials 3 and 4, the microelectrophoresis results presented in Table 7.4 and the sludge settling characteristics presented in Table 6.32, it can be concluded that, in general, the more negative the zeta potential, the better the settling characteristics, and in particular the reduction in volume occupied by the sludge. Hence, operating the Stage I reactor at a pH higher than the PZC will enhance the formation of HDS sludge.

The negative zeta potential values measured appear to encourage surface precipitation. Farley *et al.* (1985) suggested that, as a cation is complexed to the surface of a solid, a new hydroxide layer is formed on the surface, thus allowing more cations to be removed from the solution onto the surface. Farley *et al.* (1985) also suggested that, as the ratio of metal on the surface to metal in solution increases, surface precipitation becomes the dominant sorption process. This would indicate that, as HDS sludge is formed and more metals become present in the precipitated solids, heterogeneous nucleation is more likely to occur than homogeneous nucleation, thus forming a denser solid. This argument has been further developed in Chapter 8, where the mechanisms involved in the formation of Type II HDS are considered.

7.5 Scanning Electron Microscopy (SEM) Analysis

As with the XRD and zeta potential measurements, 'young' and 'old' sludge samples were taken from the continuous pilot plant during the six trials for analysis

by SEM. Single pass sludge, produced using calcium hydroxide and sodium hydroxide as the alkali reagents, was also analysed.

Two images of each sludge sample are presented (x 1,000 and x 5,000 magnification), and a scale line is overlaid onto each image for reference purposes. The SEM images were inspected manually to review the difference in morphology between 'young' and 'old' sludge and to compare the sludge generated during different trials.

7.5.1 Continuous Trial 1 (Iron in Tap Water) SEM Results

The results of the SEM analysis of Trial 1 (iron in tap water) are presented in Figure 7.13. The 'young' sludge samples are presented in Figures 7.13a (x 1,000 magnification) and 7.13b (x 5,000 magnification). Figure 7.13a shows a very dispersed image of the sludge, whilst Figure 7.13b appears to show 'soft' edges to the sludge. The average aggregation size in the 'young' sludge is approximately 1μm in diameter, with the largest aggregation being approximately 2μm in diameter (measurements are estimates from the overlaid scale).

The 'old' sludge samples are presented in Figures 7.13c (x 1,000 magnification) and 7.13d (x 5,000 magnification). Figure 7.13d shows a more compact sludge with larger aggregations and also shows that the floc aggregates are made up of several smaller aggregations. The blurred nature of Figure 7.13d is a result of the image capture and not due to the formation of the aggregates. The average aggregation size in the 'old' sludge is approximately 3μm in diameter, with the largest aggregation being approximately 6μm in diameter; and hence the 'old' sludge aggregates are approximately 3 times the size of the 'young' sludge aggregates.

No crystalline structure was apparent in any of the images presented in Figure 7.13.

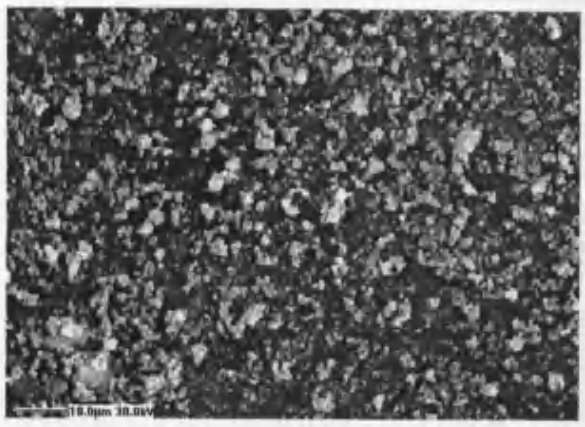


Figure 7.13a: Trial 1 (iron in tap water) SEM of 'young' sludge – Magnification 1,000

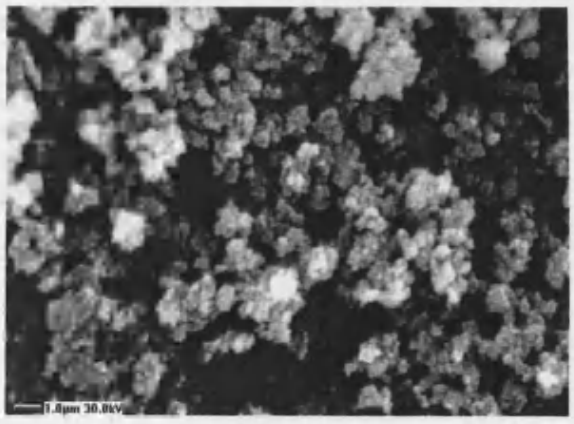


Figure 7.13b: Trial 1 (Iron in tap water) SEM of 'young' sludge – Magnification 5,000

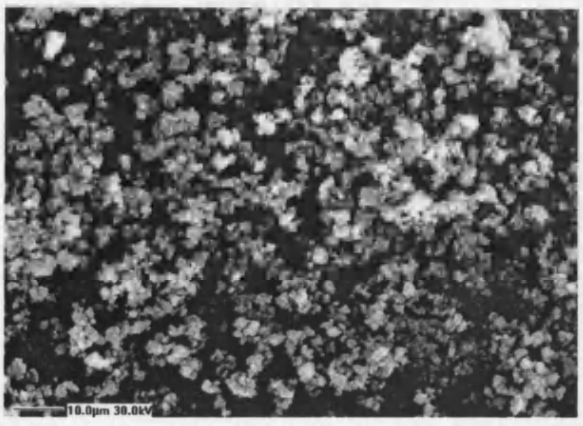


Figure 7.13c: Trial 1 (iron in tap water) SEM of 'old' sludge – Magnification 1,000

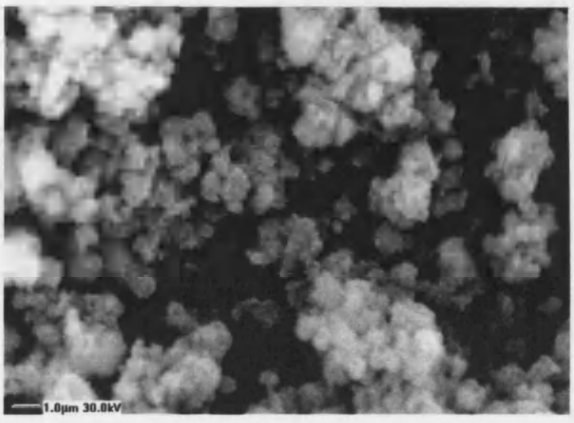


Figure 7.13d: Trial 1 (iron in tap water) SEM of 'old' sludge – Magnification 5,000

Figure 7.13: SEM images of 'young' and 'old' precipitates, by NaOH, from iron in tap water

7.5.2 Continuous Trial 2 (Zinc in Tap Water) SEM Results

The results of the SEM analysis of Trial 2 (zinc in tap water) are presented in Figure 7.14. Figure 7.14a appears to show that the aggregation of the 'young' sludge particles has started, with the aggregates already much larger than those formed in Trial 1. The average aggregation size in the 'young' sludge is approximately 10μm in diameter, with the largest aggregation being approximately 20μm in diameter. Figure 7.14b shows that the aggregates appear to be 'platy' in nature, with linkages between the aggregates.

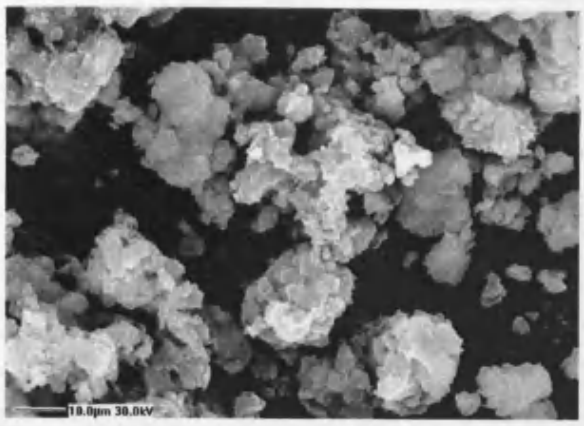


Figure 7.14a: Trial 2 (zinc in tap water) SEM of 'young' sludge – Magnification 1,000

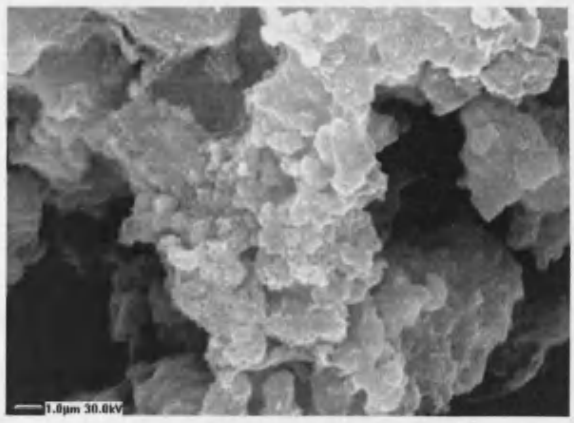


Figure 7.14b: Trial 2 (zinc in tap water) SEM of 'young' sludge – Magnification 5,000

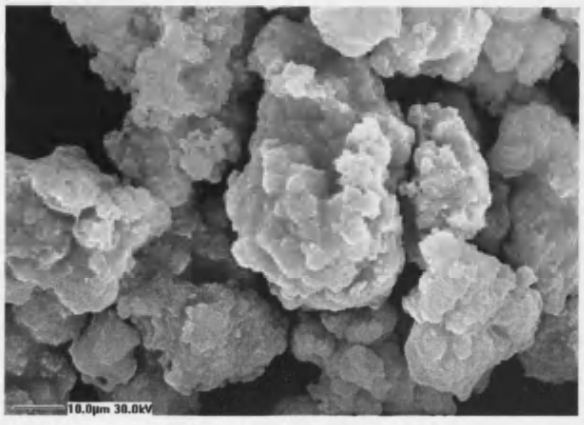


Figure 7.14c: Trial 2 (zinc in tap water) SEM of 'old' sludge – Magnification 1,000

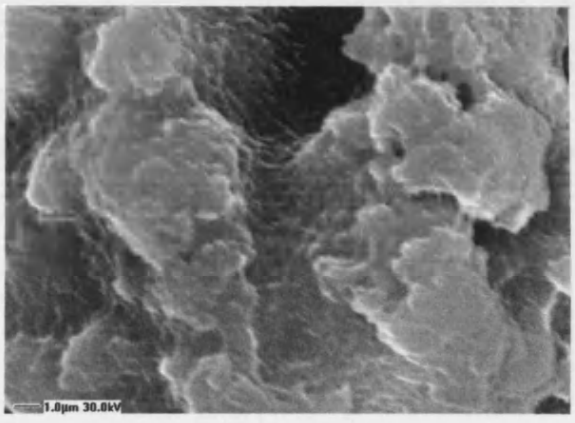


Figure 7.14d: Trial 2 (zinc in tap water) SEM of 'old' sludge – Magnification 5,000

Figure 7.14: SEM images of 'young' and 'old' precipitates, by NaOH, from zinc in tap water

Figure 7.14d shows that the 'old' sludge was more compact with massive aggregations, compared to the sludge generated in Trial 1. The average aggregation size of the 'old' sludge is approximately 25μm in diameter, with the largest aggregation being approximately 50μm in diameter; and hence the 'old' sludge aggregates are over twice the size of the 'young' zinc sludge aggregates but nearly ten times the size of the 'old' sludge generated in Trial 1. Figure 7.14d shows the plate like nature of the sludge.

As with Trial 1, no crystalline structure was apparent in any of the images presented in Figure 7.14.

7.5.3 Continuous Trial 3 (Aluminium in Tap Water) SEM Results

The 'young' sludge from Trial 3 (aluminium in tap water) is presented in Figure 7.15a and shows aggregates of the sludge particles dispersed in the general mass of the sludge.

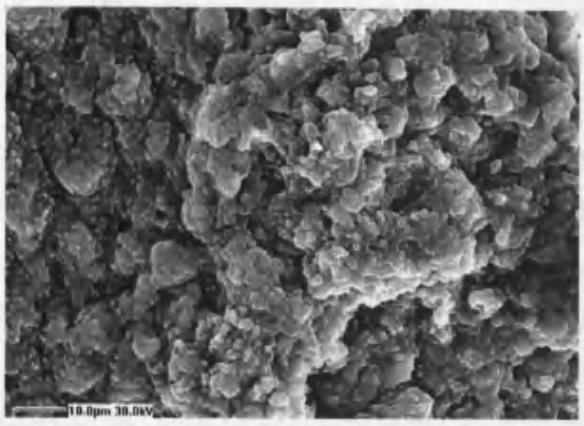


Figure 7.15a: Trial 3 (aluminium in tap water) SEM of 'young' sludge – Magnification 1,000

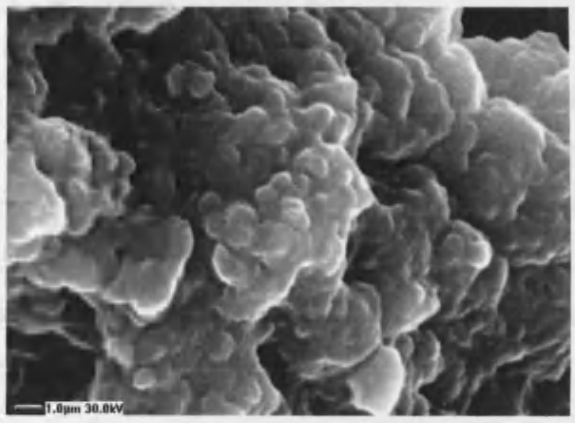


Figure 7.15b: Trial 3 (aluminium in tap water) SEM of 'young' sludge – Magnification 5,000

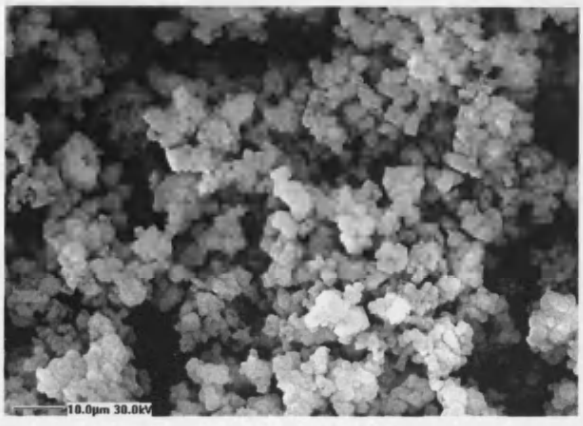


Figure 7.15c: Trial 3 (aluminium in tap water) SEM of 'old' sludge – Magnification 1,000

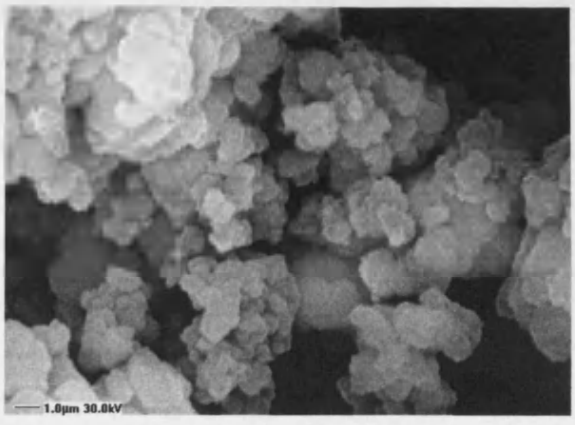


Figure 7.15d: Trial 3 (aluminium tap water) SEM of 'old' sludge – Magnification 5,000

Figure 7.15: SEM images of 'young' and 'old' precipitates, by NaOH, from aluminium in tap water

Figure 7.15b appears to show the edges of the sludge to be very 'soft' and 'smooth' in nature and also shows that the sludge particles appear to be 'welded' together in one gelatinous form. Due to the form of the sludge, it is difficult to size any of the aggregates.

Figure 7.15c shows that the 'old' sludge from Trial 3 aggregations were numerous and very compact. The average aggregation size of the 'old' sludge was approximately 5μm in diameter, with the largest aggregation being approximately 10μm in diameter. Figure 7.15d appears to show that the sludge aggregates are angular in form.

As with previous trials, no crystalline structure is apparent in any of the images presented in Figure 7.15.

7.5.4 Continuous Trial 4 (Manganese in Tap Water) SEM Results

The results of the SEM analysis of Trial 4 (manganese in tap water) are presented in Figure 7.16. Figure 7.16a shows that aggregates of the sludge particles are much more varied in size and appear to be open in nature and 'sponge-like' in appearance, which may increase the porosity of the sludge (Cornell *et al.*, 2003). The average aggregation size of the 'young' sludge was approximately 5μm in diameter, with the largest aggregation being approximately 10μm in diameter.

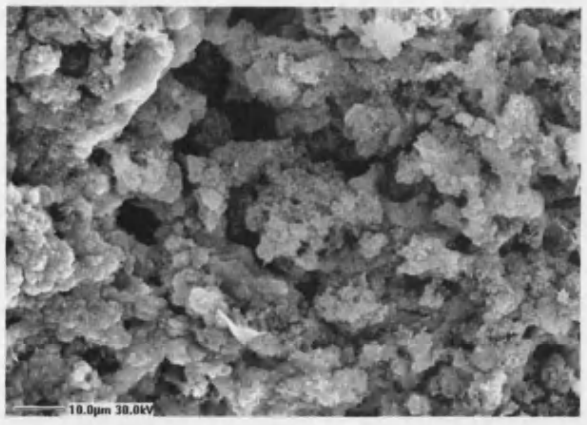


Figure 7.16a: Trial 4 (manganese in tap water) SEM of 'young' sludge – Magnification 1,000

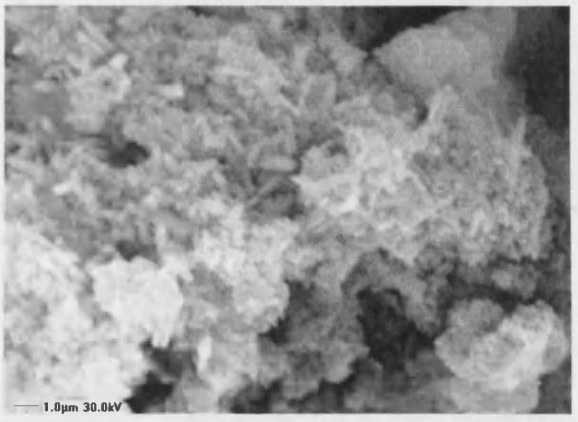


Figure 7.16b: Trial 4 (manganese in tap water) SEM of 'young' sludge – Magnification 5,000

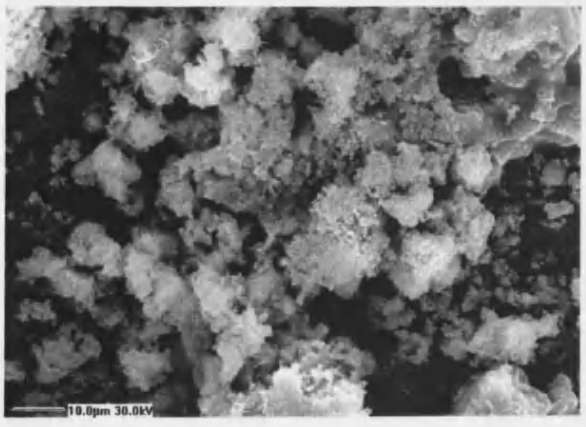


Figure 7.16c: Trial 4 (manganese in tap water) SEM of 'old' sludge – Magnification 1,000

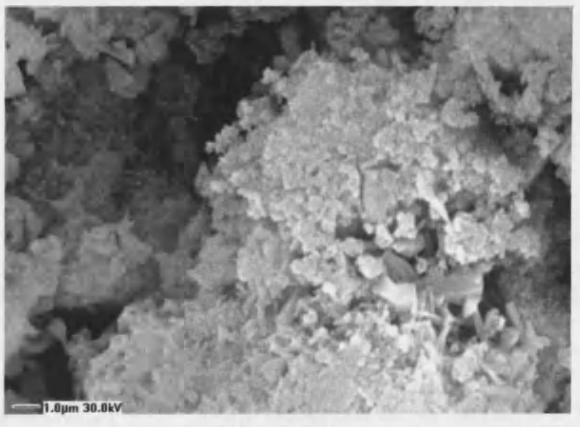


Figure 7.16d: Trial 4 (manganese in tap water) SEM of 'old' sludge – Magnification 5,000

Figure 7.16: SEM images of 'young' and 'old' precipitates, by NaOH, from manganese in tap water

Figure 7.16d shows the 'sponge-like' appearance of the sludge with some crystalline formation present. The average aggregation size of the 'old' sludge is approximately 10μm in diameter, with the largest aggregation being approximately 20μm in diameter; however, there appears to be bridging between the aggregates.

Figure 7.16d appears to show a crystalline structure forming, particularly in Figure 7.16d.

7.5.5 Continuous Trial 5 (Iron in Seawater) SEM Results

The results of the SEM analysis of Trial 5 (iron in seawater) are presented in Figure 7.17.

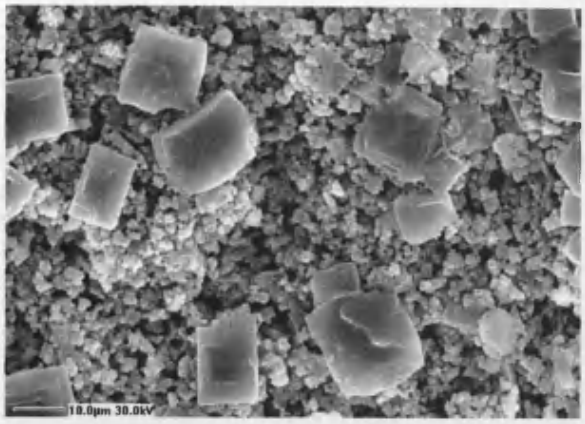


Figure 7.17a: Trial 5 (iron in seawater) SEM of 'young' sludge – Magnification 1,000

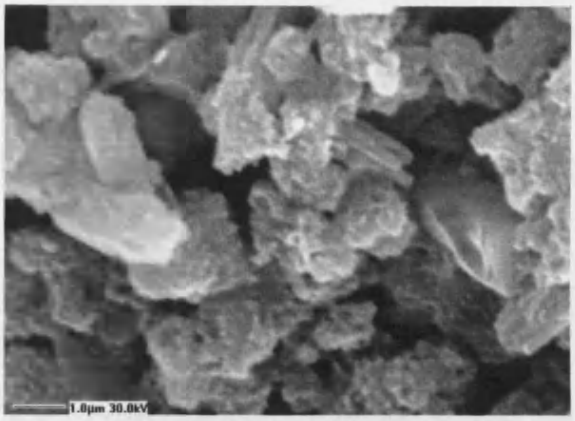


Figure 7.17b: Trial 5 (iron in seawater) SEM of 'young' sludge – Magnification 5,000

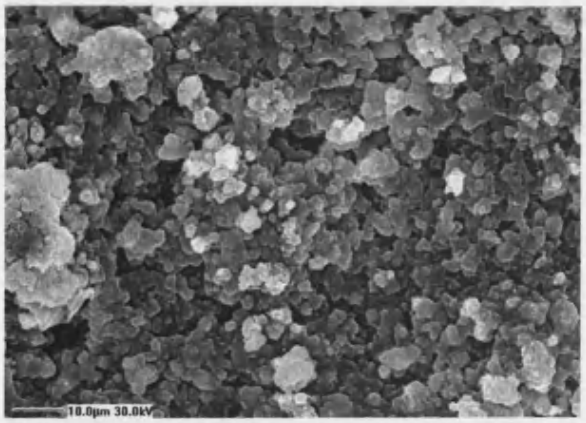


Figure 7.17c: Trial 5 (iron in seawater) SEM of 'old' sludge – Magnification 1,000

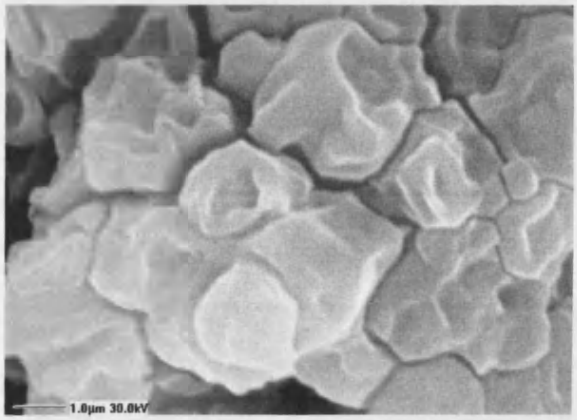


Figure 7.17: Trial 5 (iron in seawater) SEM of 'old' sludge – Magnification 5,000

Figure 7.17: SEM images of 'young' and 'old' precipitates, by NaOH, from iron in seawater

Figure 7.17a shows that large crystalline particles in a very dispersed sludge were present in the 'young' sludge formed during Trial 5, whilst Figure 7.17b shows an image of the small, dispersed sludge aggregates. The crystals are assumed to be the aragonite detected in the XRD analysis. The average size of the sludge aggregates of the 'young' sludge is approximately 2μm in diameter, with the largest aggregation being approximately 4μm in diameter; measurements are estimates from the overlaid scale.

Figure 7.17d shows that the 'old' sludge particles were very compact, with large aggregations that appeared to have formed a lattice. Figure 7.17c shows that the aggregates were made up of smaller aggregations. The average aggregation size

in the 'old' sludge is approximately 3μm in diameter, with the largest aggregation being approximately 5μm in diameter.

There is a crystalline structure in the images presented in Figure 7.17, particularly Figure 7.17a. These crystals may be the aragonite detected in the XRD analysis.

7.5.6 Continuous Trial 6 (Mixed Metals in Tap Water) SEM Results

The results of the SEM analysis of Trial 6 (mixed metals in tap water) are presented in Figure 7.18.

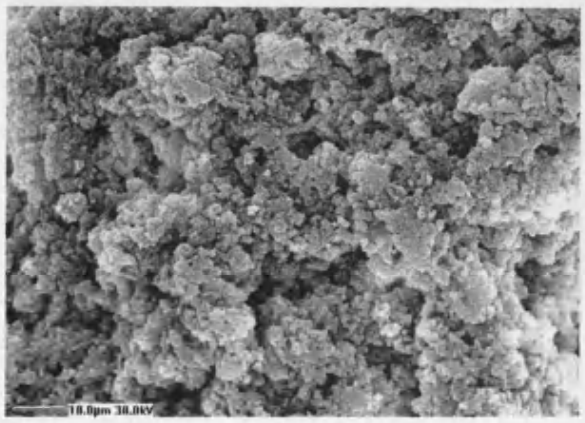


Figure 7.18a: Trial 5 (mixed metals) SEM of 'young' sludge – Magnification 1,000

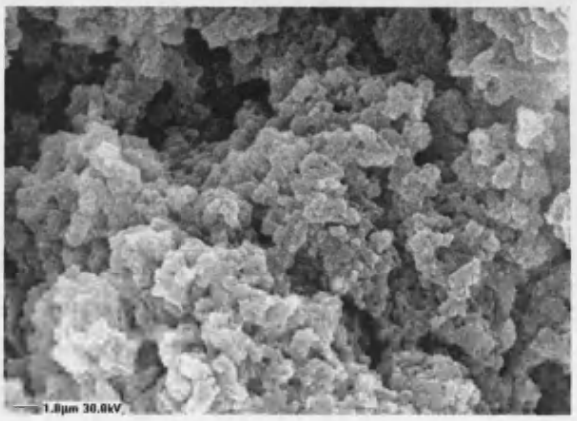


Figure 7.18b: Trial 5 (mixed metals) SEM of 'young' sludge – Magnification 5,000

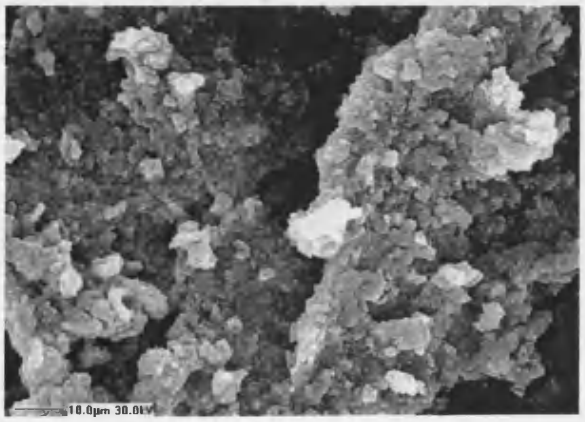


Figure 7.18c: Trial 5 (mixed metals) SEM of 'old' sludge – Magnification 1,000

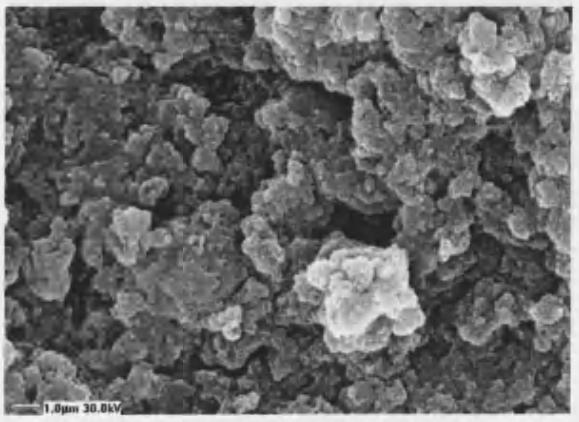


Figure 7.18d: Trial 5 (mixed metals) SEM of 'old' sludge – Magnification 5,000

Figure 7.18: SEM images of 'young' and 'old' precipitates, by $Ca(OH)_2$, from mixed metals in tap water

Figure 7.18a shows that the amorphous sludge aggregates are very dispersed. Due to the form of the sludge, it is difficult to size any of the aggregates.

Figure 7.18d again shows that the sludge was amorphous in nature. As with the 'young' sludge; sizing of the 'old' sludge aggregates, due to the form of the sludge, is not possible.

There was no crystalline structure apparent in any of the images presented in Figure 7.18.

7.5.7 Conventionally Precipitated 'Single Pass' Sludge SEM Results

The results of the SEM analysis of conventionally precipitated single pass sludge (produced using calcium hydroxide and sodium hydroxide) are presented in Figure 7.19.

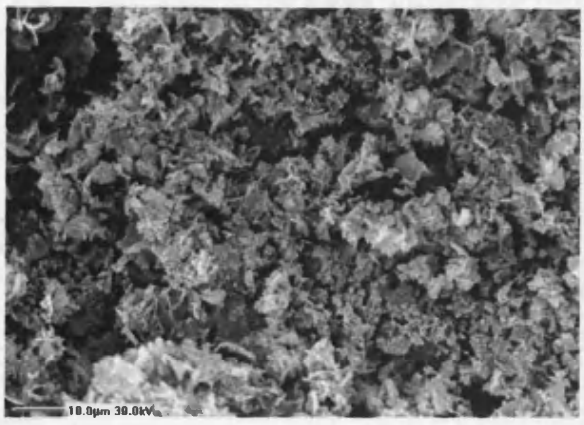


Figure 7.19a: 'Single pass' sludge $Ca(OH)_2$ sludge – Magnification 1,000

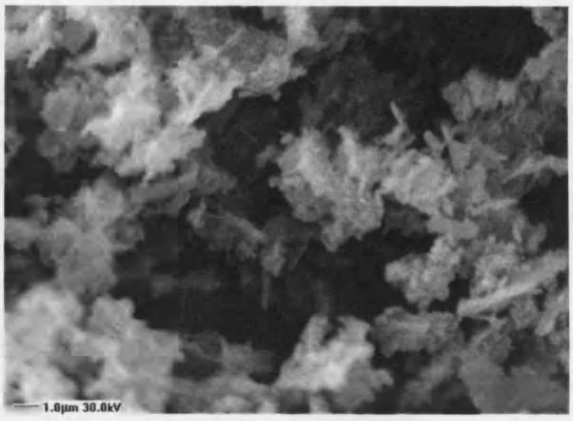


Figure 7.19b: 'Single pass' sludge $Ca(OH)_2$ sludge – Magnification 5,000

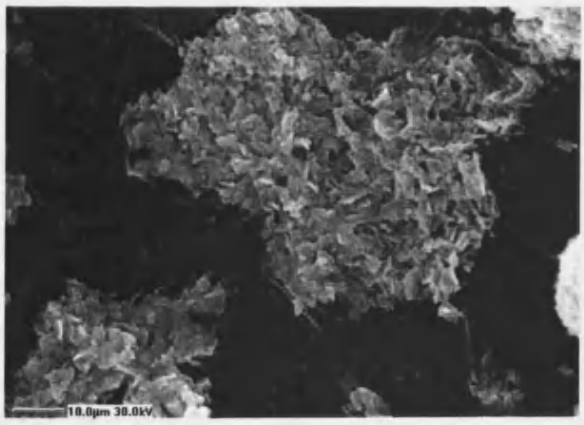


Figure 7.19c: 'Single pass' sludge NaOH sludge – Magnification 1,000

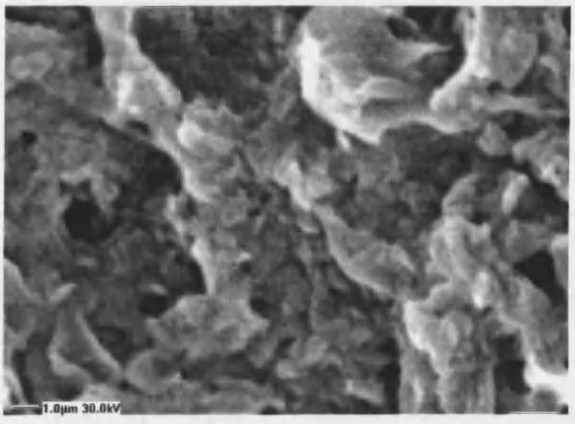


Figure 7.19d: 'Single pass' sludge NaOH sludge – Magnification 5,000

Figure 7.19: SEM images of 'single pass' precipitates, by $Ca(OH)_2$ and NaOH, from iron in tap water

The minewater used for the production of these precipitates was a synthetic minewater, with an initial iron concentration of 200 mg/l of iron and the iron added as Fe (II) chloride.

Figure 7.19a shows that the aggregates, were 'flaky' in appearance, when calcium hydroxide was used as the alkali reagent, whilst Figure 7.17b shows that the 'flakes' were very fine in nature. Due to the form of the sludge, it is difficult to size

any of the aggregates.

Figure 7.19c, when sodium hydroxide was used as the alkali reagent, shows a very large amorphous sludge aggregation, and very 'open' in nature. Figure 7.19d shows that the sludge particles appear to be gelatinous in form. The sludge presented in Figure 7.19c is massive in size at approximately 70μm in diameter.

There was no crystalline structure in the images presented in Figure 7.19.

7.5.8 Summary of SEM Analysis

A summary of the SEM analysis is presented in Table 7.5.

Table 7.5: Comparison of SEM analysis of all sludges analysed

Trial Number	'Young' sludge		'Old' sludge		Comments on aggregates
	Average size μm	Maximum size μm	Average size μm	Maximum size μm	
Trial 1 - Iron in tap water	1	2	3	6	Fine, small and dispersed
Trial 2 - Zinc in tap water	10	20	25	50	Platy, massive
Trial 3 - Aluminium in tap water	-	-	5	10	Small, compact, angular, fused together
Trial 4 - Manganese in tap water	5	10	10	20	Sponge like, larger aggregates, small crystals, open
Trial 5 – Iron in seawater	2	4	3	5	Fine, lattice formed, aragonite crystals
Trial 6 – Mixed metals	-	-	-	-	Fine dispersed, very amorphous
Wheal Jane Sludge (16 Aug 01)	4	8	N/A	N/A	Dispersed, amorphous, calcite crystals
Wheal Jane Sludge (10 Feb 05)	4	8	N/A	N/A	Dispersed, amorphous, calcite crystals
$Ca(OH)_2$ sludge	-	-	N/A	N/A	Flaky, fine
NaOH sludge	-	-	N/A	N/A	Amorphous, open

The aggregates produced during Trial 3 (aluminium in tap water) were small and very compact and appeared dense. The 'young' sludge from Trial 3 appeared to be welded together and to be gelatinous in nature. This would account for the poor initial settling characteristics of the sludge. The 'old' sludge for Trial 3 appeared to be angular in form. Trial 6 (iron in seawater) sludge appeared to be similar in characteristics to the sludge produced in Trial 3.

Trial 2 (zinc in tap water) produced the sludge with the largest aggregations, which were 'platy' in nature. The large size of the aggregations improved the dewatering characteristics, described Section 7.7.1, and could explain the high settlement velocities of the sludge generated in Trial 2, presented Table 6.31.

Trial 4 (manganese in tap water) produced sludge that appeared to be open in structure and 'sponge-like' in nature, giving rise to a large surface area and allowing surface precipitation to occur, as described in Section 7.4.9. Trial 4 generated a solid with good settling characteristics, enabling a good reduction in sludge volume, as presented in Table 6.32. It is therefore suggested that heterogeneous nucleation is fundamental to the forming of HDS sludge. As the larger particles of Trials 2 and 4 had better sludge settlement characteristics than the smaller particles of Trial 3, it is that suggested heterogeneous nucleation is more important than the aggregation of the smaller floc particles.

The sludge aggregates produced when iron was present in the pilot plant feed were very small and dispersed. The maximum size of the aggregates in Trial 1 and Trial 5 was 6μm. These were slightly smaller than the aggregates formed at the Wheal Jane MWTP shown in Figure 4.36.

The conventionally precipitated 'single pass' sludge was amorphous and 'light' in appearance. However, the calcium hydroxide sludge appeared fine and flaky, whilst the sodium hydroxide sludge was very open. Trial 1 (iron in tap water) produced a much denser, more compact sludge in comparison to the 'single pass' sludge. The appearance of the sludge generated at the Wheal Jane MWTP was similar to that generated during Trial 1 (iron in tap water).

7.6 Transmission Electron Microscopy (TEM) Analysis

Transmission Electron Microscopy (TEM) analysis was undertaken on 'young' and 'old' HDS sludge samples taken during Trial 1 (iron in tap water) and 'single pass' sludge, produced using sodium hydroxide as the alkali reagent (see Section 3.5.4).

Two images of each sludge sample are presented (x 6,500 and x 42,000 magnification) and a scale line is overlaid onto each image for reference purposes. The TEM images were inspected manually to review the difference in morphology between 'young' and 'old' HDS sludge and the 'single pass' conventionally

precipitated sludge. The minewater used for the production of the 'single pass' precipitates was a synthetic minewater, with an initial iron concentration of 200 mg/l of iron with the iron added as Fe (II) chloride.

7.6.1 TEM Analysis Results

The results of the TEM analysis undertaken on the three sludges are presented in Figure 7.20.

The 'single pass' sludge TEM images are presented in Figures 7.20a (x 6,500 magnification) and 7.20b (x 42,000 magnification). Figure 7.20a shows a very dispersed image of the sludge, in which several large dense precipitates can be seen. Figure 7.20b would appear to show 'soft' edges to the sludge, however on close examination the precipitates appear to resemble cotton wool. The average size of the individual aggregations in the 'single pass' sludge is approximately 0.1μm in diameter (measurements are estimates from the overlaid scale), whilst the large dense particles average 2μm in diameter.

The 'young' Trial 1 HDS sludge samples are presented in Figures 7.20c (x 6,500 magnification) and 7.20d (x 42,000 magnification). Figure 7.20c appears to show a less dispersed sludge with increased sharpness to the edges of the sludge and again large dense sludge particles can be seen. Figure 7.20c indicates more structure to the flocs compared to the Figure 7.20a, and have the appearance of folded paper. There is more aggregation of the particles compared to the 'single pass' sludge that makes sizing of the particles impossible.

The 'old' Trial 1 HDS sludge samples are presented in Figures 7.20e (x 5,000 magnification) and 7.20f (x 1,000 magnification). Figure 7.20e shows a more compact sludge (compared to Figures 7.20a and 7.20c) with larger aggregations. Figure 7.20f shows that the aggregates are made up of smaller aggregates and particles that resemble folded foil. The floc particles appear very dense, with Figure 7.20f showing the floc structure, which appears to be crystalline in nature.

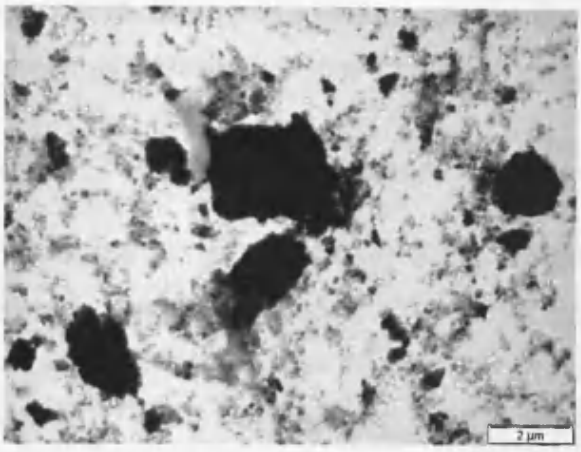


Figure 7.20a: TEM of 'single pass' precipitates, by NaOH, from iron in tap water – Magnification 6500x

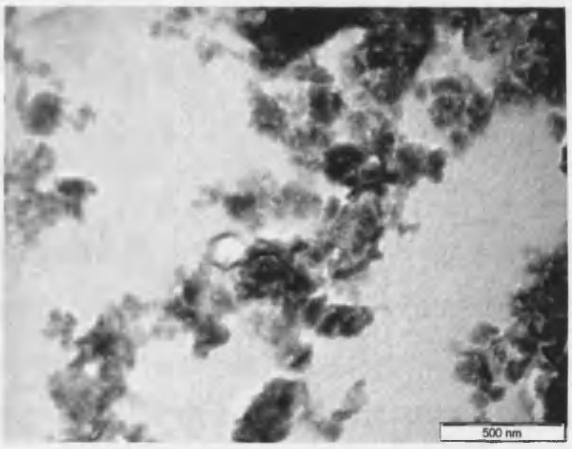


Figure 7.20b: TEM of 'single pass' precipitates, by NaOH, from iron in tap water – Magnification 42000x

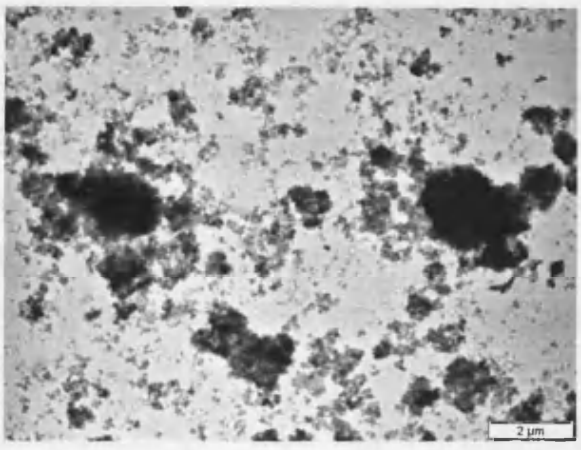


Figure 7.20c: TEM of 'young' HDS precipitates, by NaOH, from iron in tap water – Magnification 6500x

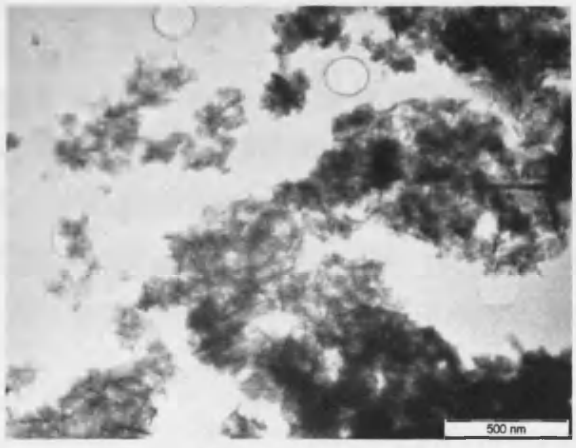


Figure 7.20d: TEM of 'young' HDS precipitates, by NaOH, from iron in tap water – Magnification 42000x

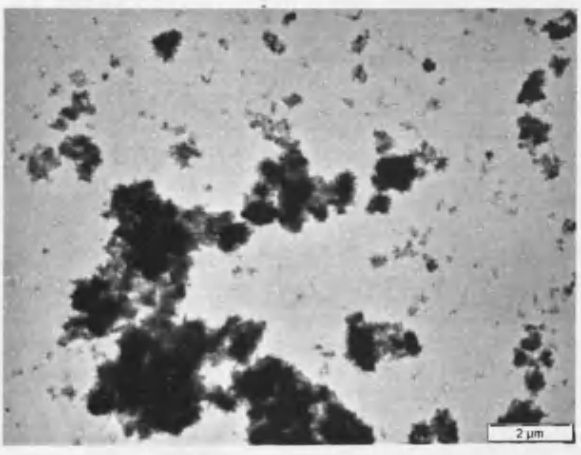


Figure 7.20e: TEM of 'old' HDS precipitates, by NaOH, from iron in tap water – Magnification 6500x

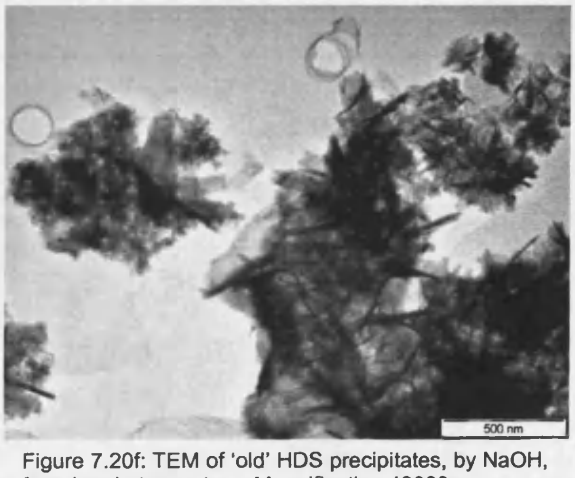


Figure 7.20f: TEM of 'old' HDS precipitates, by NaOH, from iron in tap water – Magnification 42000x

Figure 7.20: TEM images of HDS and 'single pass' precipitates, by NaOH, from iron in tap water

7.7 Sludge Dewatering Characteristics

As sludge ages and changes its mineralogy and morphology, or is generated by different processes, the dewatering characteristics of the sludge can also change. Sludge samples taken at the end of each trail was subjected to sludge filtration

tests and sludge centrifuge tests to develop an understanding of how the dewatering characteristics of sludge differed in each trial.

7.7.1 Filtration Results and Discussion

Filtration trials (see Section 3.4.5 for methodology) were undertaken on the final sludges generated during the six continuous pilot plant trials and conventionally precipitated single pass sludge (using sodium hydroxide as the alkali reagent). As a comparison, sludge from a HDS plant in the north east of England (Horden MWTP, where high levels of calcium carbonate are precipitated due to inflated concentrations of carbon dioxide in the minewater) was also subjected to testing.

Plotted in Figure 7.21 are the filtrate volumes against time for each of the sludges tested. This shows that the 'single pass' sludge took longest to filter a given volume. The improved filtration characteristics of the HDS sludge compared to the single pass sludge would have a practical effect of reducing the size of any dewatering equipment that would be required and the time it takes to dewater the sludge.

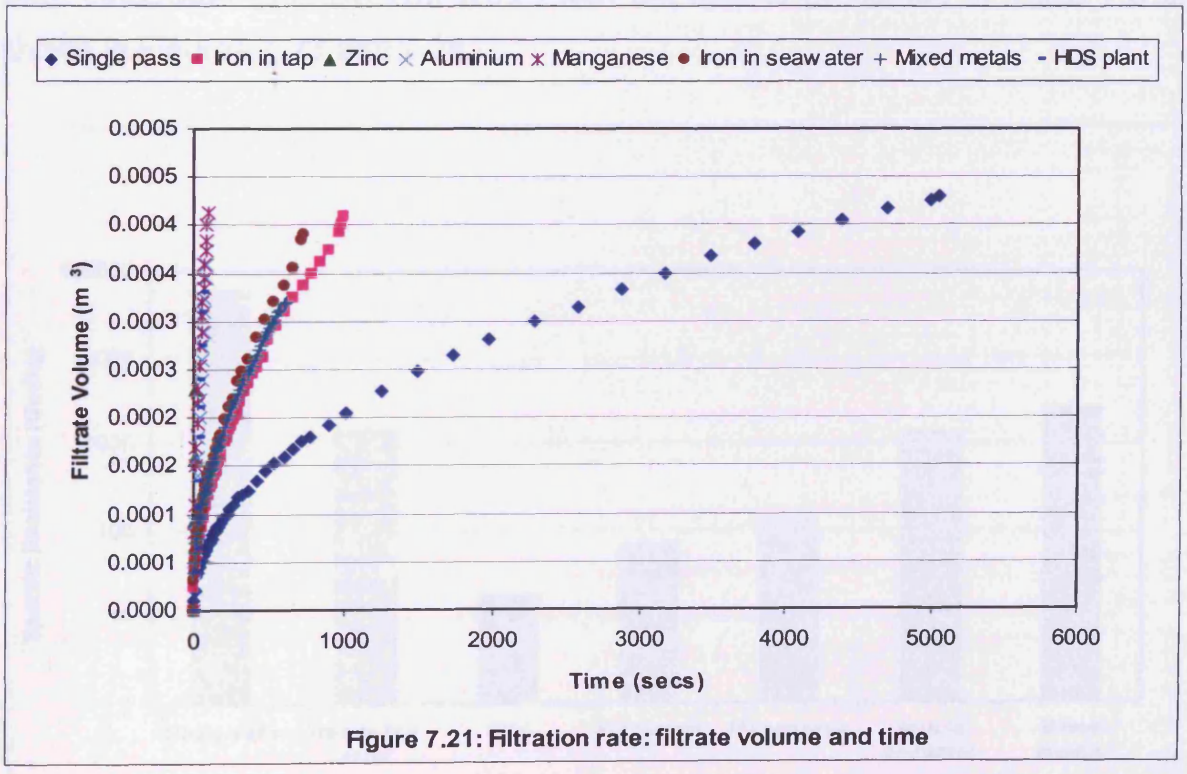


Figure 7.21: Filtration rate: filtrate volume and time

Plotted in Figure 7.22 are the ratios of time and filtrate volumes against filtrate volumes for each of the sludges tested. This shows that the 'single pass' sludge had the highest slope of all the sludges and indicates that the HDS process

increases the filterability of the sludge.

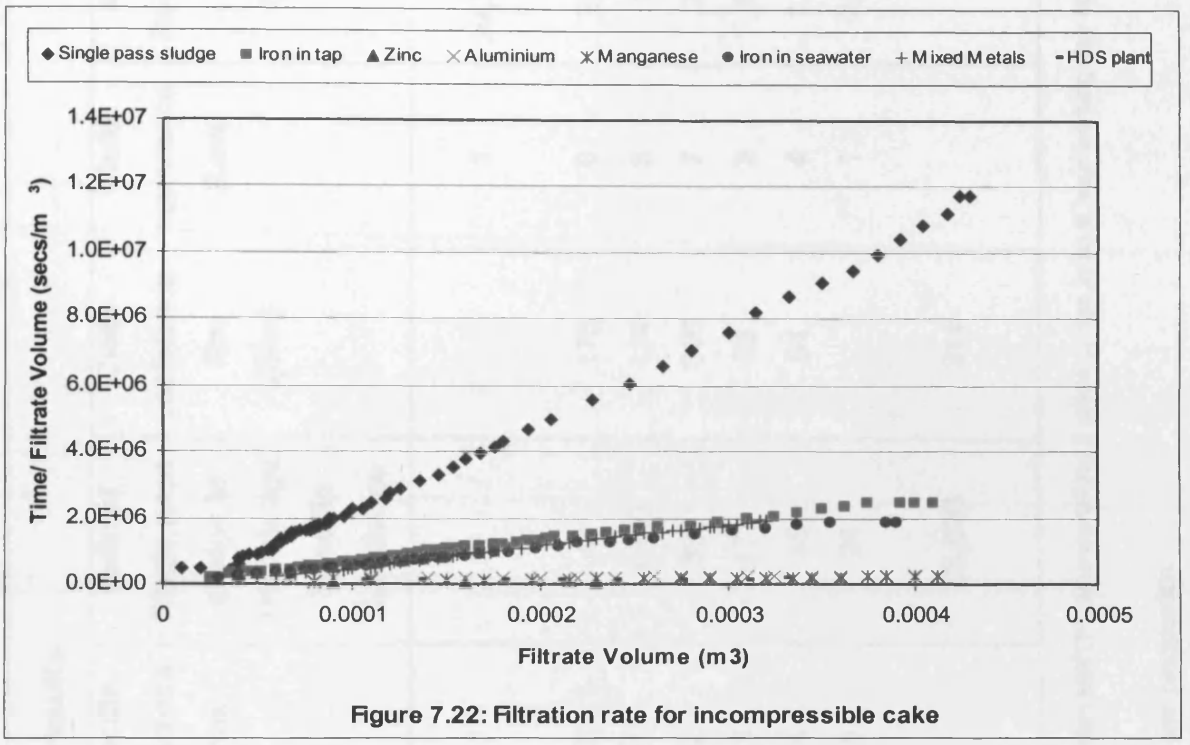


Figure 7.22: Filtration rate for incompressible cake

The specific cake resistances and cloth resistances for each of the sludges tested were calculated (see Section 3.5.5) with the results presented in Table 7.6 and shown in Figures 7.23 and 7.24.

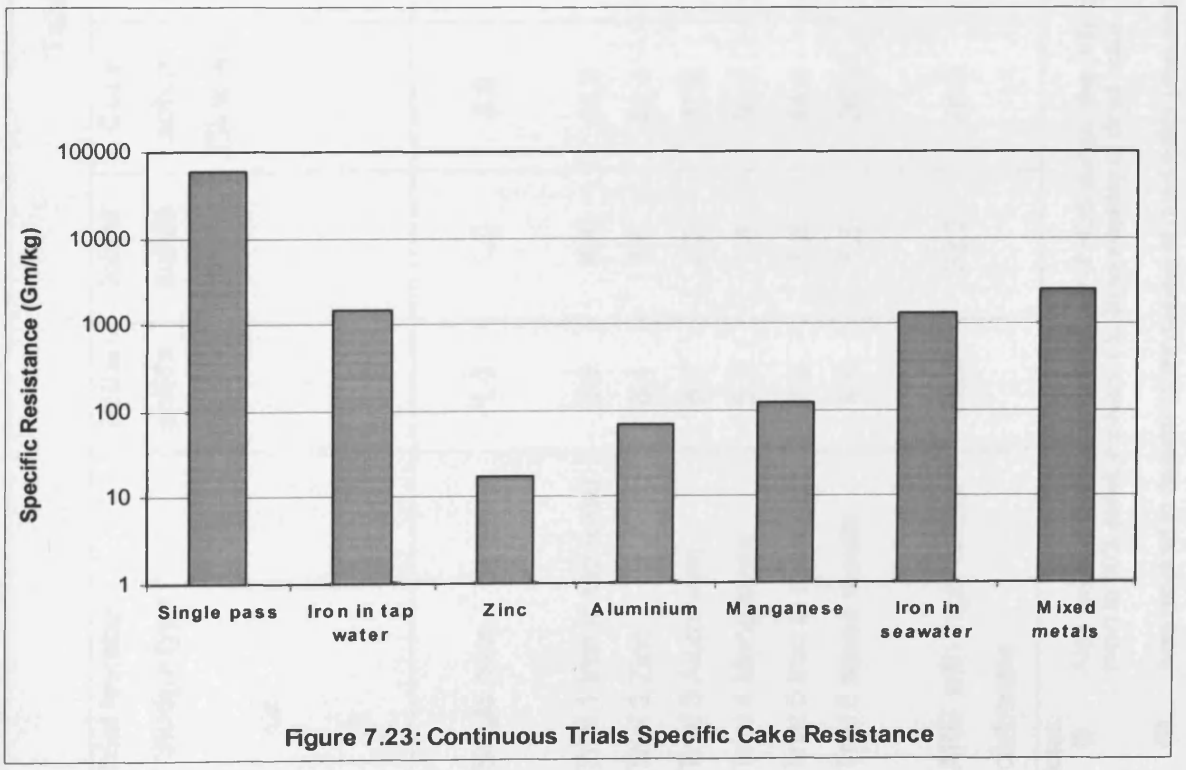


Figure 7.23: Continuous Trials Specific Cake Resistance

Table 7.6: Filtration results

Trial Number / Sludge type	Initial solids (% w/v)	Initial solids (% w/w)	Cake solids (% w/w)	Specific resistance α (Gm/kg)	Specific resistance Rank	Ratio of Single pass sludge to Trial sludge Specific Resistance	Cloth resistance Rm (G/m)	Cloth resistance Rank	Area Required (i) (m^2)
Single pass	1.0	1.0	8.9	52,800	7	1	-	1	29,300 (ii)
Trial 1 Iron in tap water	8.9	8.4	44.5	1,230	5	41	176	6	2,040
Trial 2 Zinc	8.4	7.9	42.4	15	1	3,450	114	5	182
Trial 3 Aluminium	8.7	8.2	37.6	58	2	839	310	7	333
Trial 4 Manganese	8.2	7.8	50.7	110	3	477	73	3	599
Trial 5 Iron in seawater	8.0	7.6	44.0	1,130	4	45	94	4	1,990
Trial 6 Mixed metals	5.5	5.3	26.3	2,050	6	24		1	2,900
ARD with high calcium carbonate	39.6	32.3	76.3	1		35,600	314		14

Notes:

(i) Area required to dewater 180 m^3/day of HDS sludge (the daily sludge generation at Horden MWTP) by undertaking 2 press cycles in an 8 hour working day from 15% (w/w) to 50% (w/w), equivalent to 30 tonnes/day of dried solids.

(ii) Area required to dewater 30 tonnes/day of dried solids produced by conventional 'single pas' precipitation.

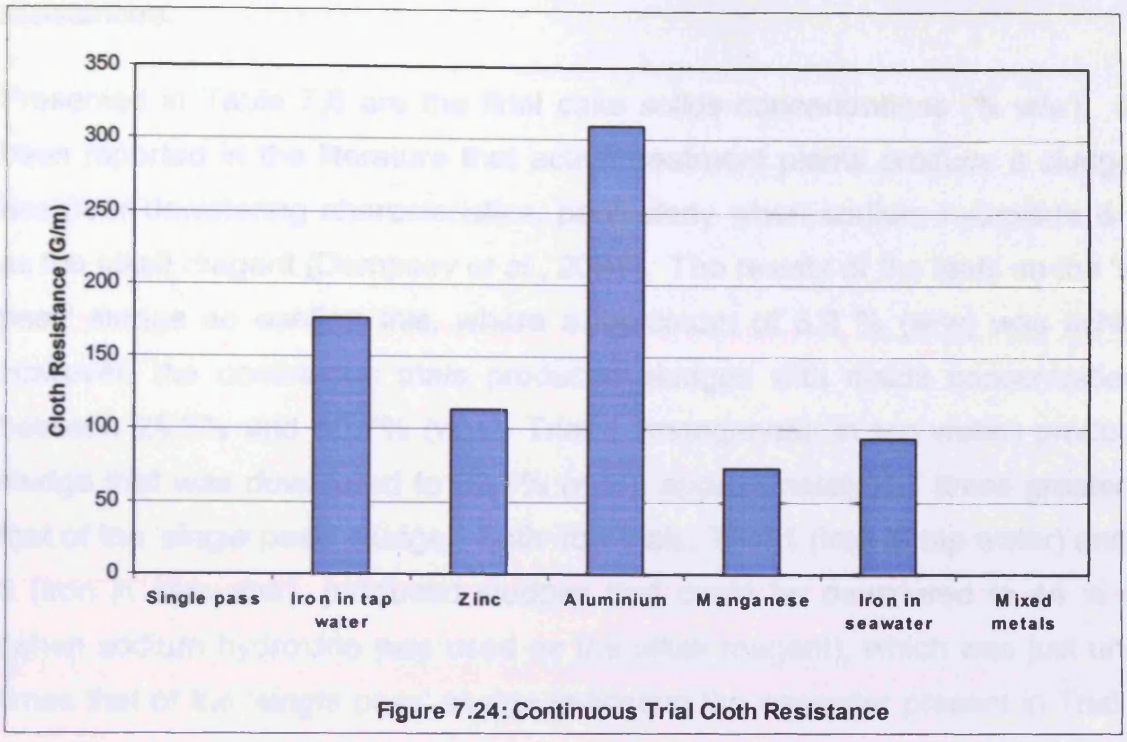


Figure 7.24: Continuous Trial Cloth Resistance

Trial 2 (zinc in tap water) produced the sludge with the lowest specific cake resistance of 15 Gm/kg, whilst the 'single pass' sludge had the highest specific cake resistance at 52,800 Gm/kg. The Trial 2 sludge had a cake resistance 3,450 times lower than that of the 'single pass' sludge.

The sludges from Trial 3 (aluminium in tap water) and Trial 4 (manganese in tap water) had the next lowest cake resistance of 70 Gm/kg and 123 Gm/kg respectively. The Trial 3 results were unexpected, as all other tests indicated a sludge of poor settling and compaction characteristics.

The two iron trials, Trial 1 (iron in tap water) and Trial 5 (iron in seawater), produced sludge of similar specific cake resistances of 1,230 Gm/kg and 1,130 Gm/kg respectively. The Trial 1 specific cake resistance was approximately 41 times lower than that of the 'single pass' sludge when identical synthetic mine water was trialled.

Of the sludges produced during the continuous trials, the sludge generated during Trial 6 (mixed metals) had the highest specific cake resistance at 2,050 Gm/kg.

As a comparison, the sludge generated by the HDS minewater treatment plant in the north east of England (Horden MWTP) had a specific cake resistance of 1 Gm/kg.

The cloth resistances were ranked generally in reverse order to the specific cake

resistances.

Presented in Table 7.6 are the final cake solids concentrations (% w/w). It has been reported in the literature that active treatment plants produce a sludge that has poor dewatering characteristics, particularly when sodium hydroxide is used as the alkali reagent (Dempsey *et al.*, 2001). The results of the tests on the 'single pass' sludge do confirm this, where a maximum of 8.9 % (w/w) was achieved. However, the continuous trials produced sludges with solids concentrations of between 26.3% and 50.7% (w/w). Trial 4 (manganese in tap water) produced a sludge that was dewatered to 50.7% (w/w), approximately 4.7 times greater than that of the 'single pass' sludge. Both iron trials, Trial 1 (iron in tap water) and Trial 5 (iron in seawater), produced sludges that could be dewatered to 44 % (w/w) (when sodium hydroxide was used as the alkali reagent), which was just under 4 times that of the 'single pass' sludge indicating the seawater present in Trial 5 did not affect the dewatering characteristics of the sludge formed.

By rearranging Equation 3.1 and knowing the specific cake and cloth resistances, it is possible to calculate the area requirements to dewater a given sludge volume. Presented in Table 7.6 are the plate area requirements of a press dewatering 180 m^3 of sludge with an initial HDS sludge feed concentration of 15% (w/w) and a required dewatered cake concentration of 50% (w/w) (the dewatering requirements at Horden MWTP), and assumes the press is operated using 2 press cycles in an 8 hour working day. For the 'single pass' sludge feed a sludge concentration of 5% (w/w) has been used. These results indicate that a sludge press approximately 14.5 times smaller would be required to dewater the sludge generated when an iron based minewater was treated by the HDS process rather than treated by conventional 'single pass' minewater treatment.

Therefore, it can be seen that the HDS process greatly improves the sludge dewaterability of the sludge produced by active treatment of minewater, even when sodium hydroxide is used as the alkali reagent.

7.7.2 Centrifuge Test Results and Discussion

A common means of dewatering sludge is by centrifuging; therefore, sludge generated throughout the trials was subjected to dewatering tests by bench centrifuge (see Section 3.4.6 for methodology).

Figure 7.25 presents the results for the centrifuge tests on the sludge generated during Trial 1 (iron in tap water), showing solids concentration plotted against g (i.e. 1, 500, 1000, 1500 and 2000 g).

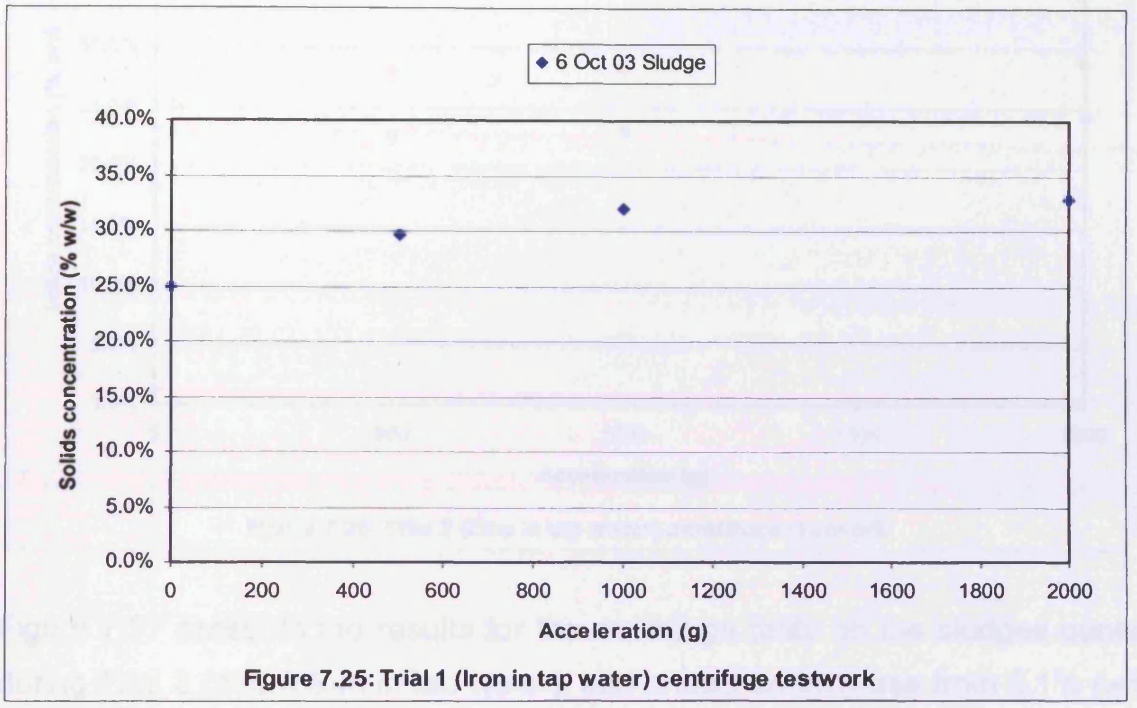


Figure 7.25: Trial 1 (Iron in tap water) centrifuge testwork

Figure 7.25 shows that operating the bench centrifuge at 2000g increased the sludge solids concentration from 25% (w/w) to 33% (w/w). The maximum solids concentration achieved was 33% (w/w) at the end of the test work when the centrifuge was running at 2000 g, however this was only 1% (w/w) higher than when the centrifuge was run at 1000g.

Two samples of sludge from Trial 2 (zinc in tap water) were tested using the centrifuge, with Figure 7.26 showing an increase from 18% w/w to 24% (w/w) and from 25% (w/w) to 29% (w/w) for the sludges removed on the 25 November 2003 and the 28 November 2003 respectively. Figure 7.26 also shows that, as the sludge aged, the maximum solids concentration achievable increased. The maximum solids concentration achieved was 29% (w/w) by the sludge removed on the 28th November 2003.

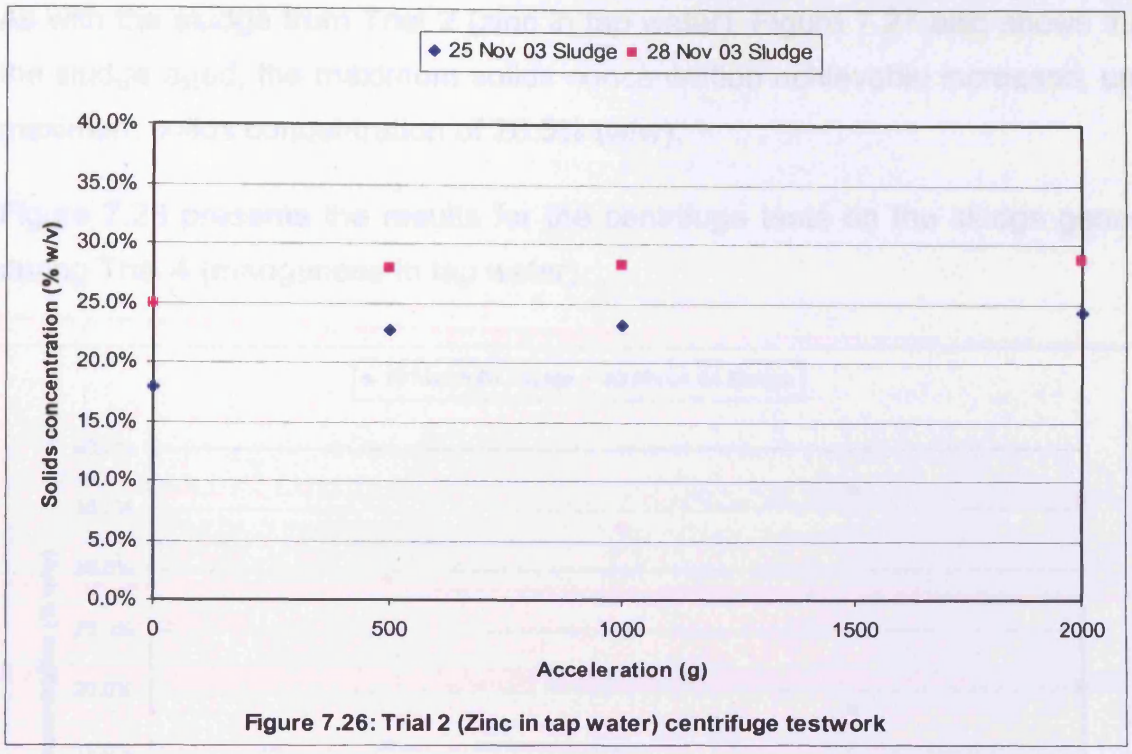


Figure 7.26: Trial 2 (Zinc in tap water) centrifuge testwork

Figure 7.27 presents the results for the centrifuge tests on the sludges generated during Trial 3 (aluminium in tap water), and shows an increase from 3.1% (w/w) to 8.8% (w/w), from 5.7% (w/w) to 12.7% (w/w), from 13.4% (w/w) to 25.6% (w/w) and from 14.1% (w/w) to 26.5% (w/w) in the solids concentration for the four sludge samples respectively.

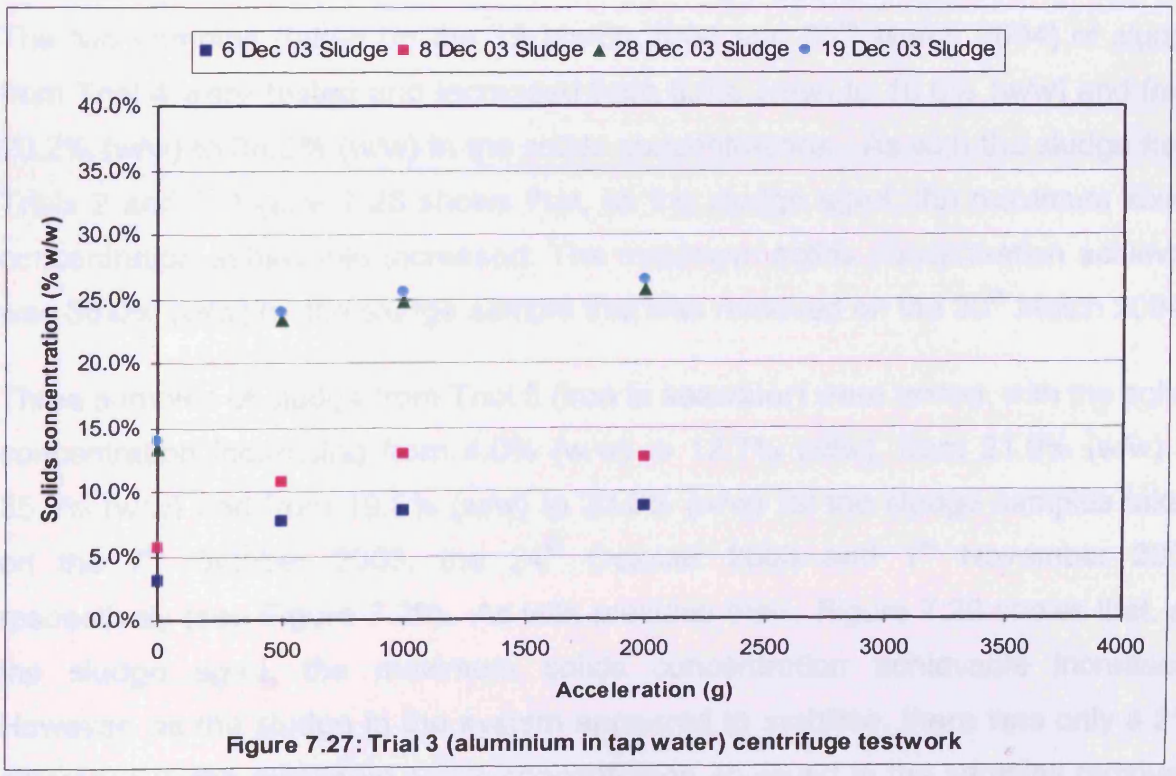


Figure 7.27: Trial 3 (aluminium in tap water) centrifuge testwork

As with the sludge from Trial 2 (zinc in tap water), Figure 7.27 also shows that as the sludge aged, the maximum solids concentration achievable increased, up to a maximum solids concentration of 26.5% (w/w).

Figure 7.28 presents the results for the centrifuge tests on the sludge generated during Trial 4 (manganese in tap water).

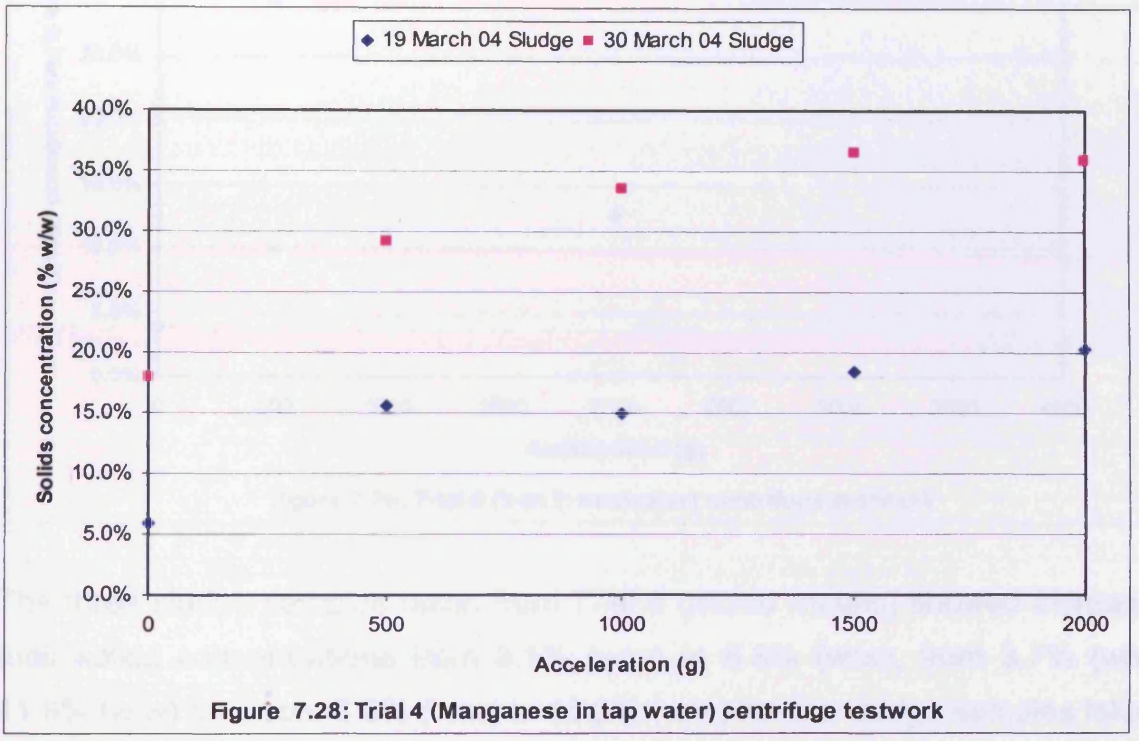


Figure 7.28: Trial 4 (Manganese in tap water) centrifuge testwork

The two samples (taken on the 19 March 2004 and 30th March 2004) of sludge from Trial 4 were tested and increased from 5.9% (w/w) to 18.0% (w/w) and from 20.2% (w/w) to 36.0% (w/w) in the solids concentrations. As with the sludge from Trials 2 and 3, Figure 7.28 shows that, as the sludge aged, the maximum solids concentration achievable increased. The maximum solids concentration achieved was 36.0% (w/w) by the sludge sample that was removed on the 30th Match 2004.

Three samples of sludge from Trial 5 (iron in seawater) were tested, with the solids concentration increasing from 4.0% (w/w) to 12.7% (w/w), from 21.0% (w/w) to 35.0% (w/w) and from 19.8% (w/w) to 33.0% (w/w) for the sludge samples taken on the 7th October 2003, the 24th October 2003 and 1st November 2003 respectively (see Figure 7.29). As with previous trials, Figure 7.29 shows that, as the sludge aged, the maximum solids concentration achievable increased. However, as the sludge in the system appeared to stabilise, there was only a 2% difference in the maximum solids concentration achieved in the samples removed on the 24th October 2003 (33% w/w) and 1st November 2003 (35 % w/w)

respectively.

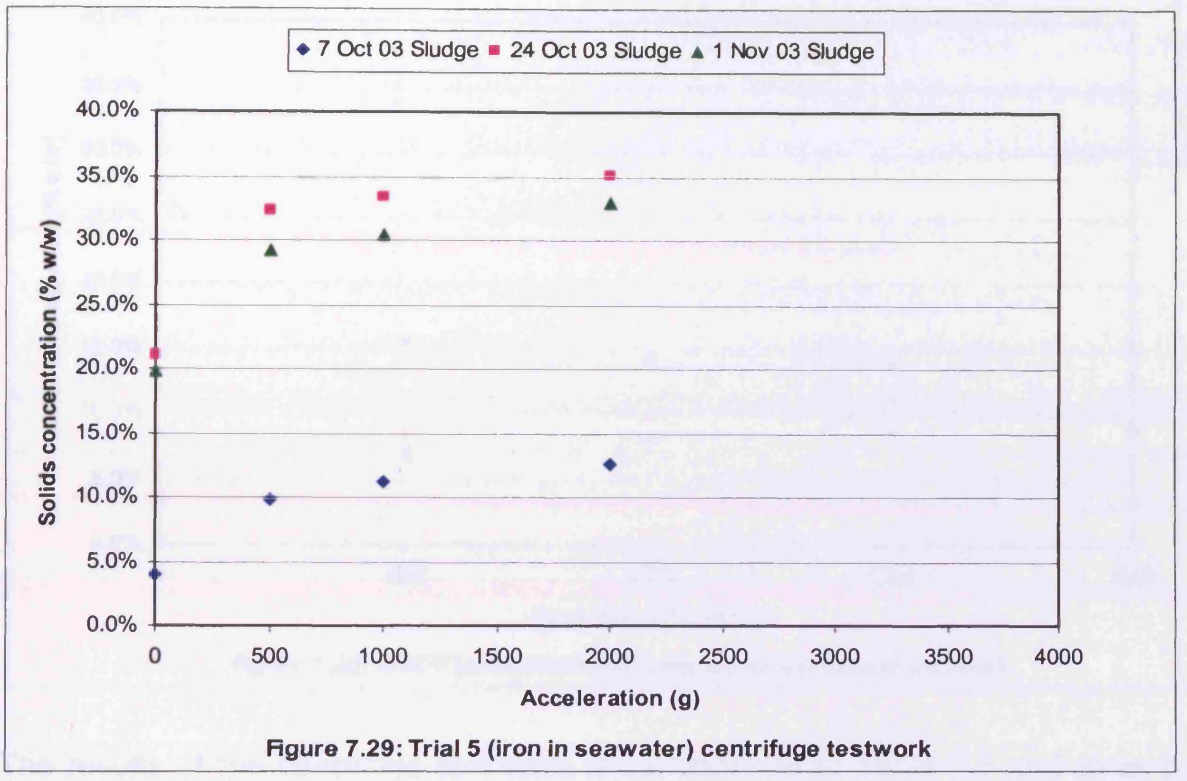


Figure 7.29: Trial 5 (iron in seawater) centrifuge testwork

The three sludge samples taken from Trial 6 (mixed metals) showed increases in their solids concentrations from 3.1% (w/w) to 8.8% (w/w), from 3.7% (w/w) to 11.8% (w/w) and from 8.6% (w/w) to 15.2% (w/w) for the sludge samples taken on the 24th February 2004, 1st March 2004 and 5th March 2004 respectively. As with previous trials, Figure 7.30 shows that, as the sludge aged, the maximum solids concentration achievable increased however, the increases are small in comparison to previous trials. The maximum solids concentration achieved was 15.0% (w/w) by the sludge sample that was removed on the 5th March 2004.

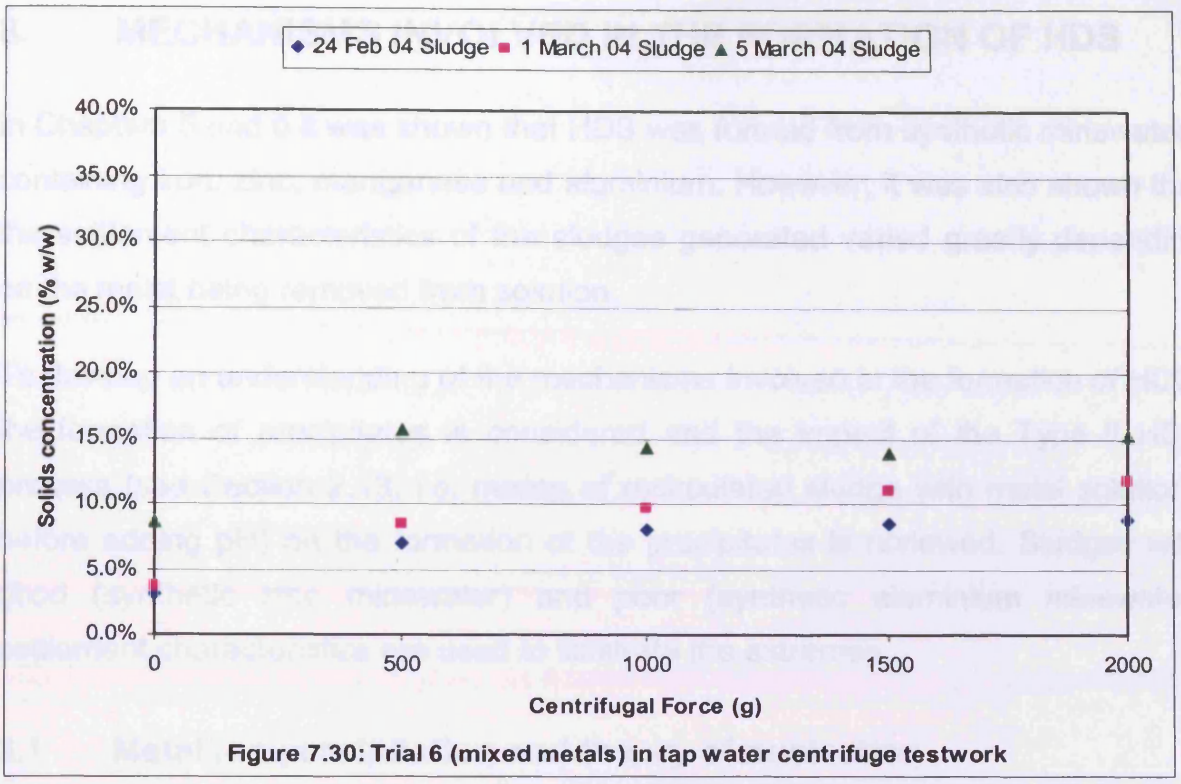


Figure 7.30: Trial 6 (mixed metals) in tap water centrifuge testwork

The results of the centrifuge test work is summarised in Table 7.7 and show the sludges that achieved the maximum consolidation from each trial.

Table 7.7: Centrifuge dewatering results

Trial Number	Sludge type	Units	Centrifuge acceleration (g)				
			1	500	1000	1500	2000
Trial 1	Iron in tap water	(% w/w)	24.9	29.6	32.1		32.9
Trial 2	Zinc	(% w/w)	25.0	27.9	28.2		28.8
Trial 3	Aluminium	(% w/w)	14.1	24.0	25.5		26.5
Trial 4	Manganese	(% w/w)	17.2	29.2	33.6	36.5	36.0
Trial 5	Iron in sweater	(% w/w)	21.1	32.3	33.4		35.1
Trial 6	Mixed metals	(% w/w)	8.6	15.6	14.3	14.0	15.2

The sludge generated during Trial 4 (manganese in tap water) produced the sludge with the highest final solids concentration, 33.6% (w/w). Of the sludges that produced the highest final solids concentration, Trial 3 (aluminium in tap water) sludge had the greatest increase in solids concentration due to centrifuging.

As with the filtration tests, the HDS process improves the sludge dewaterability and the maximum final solids concentration achievable. However, in comparison to the filtration tests, the final solids concentrations were lower, suggesting that pressing the sludge produces a product with a higher final solids concentration.

8 MECHANISMS INVOLVED IN THE FORMATION OF HDS

In Chapters 5 and 6 it was shown that HDS was formed from synthetic minewaters containing iron, zinc, manganese and aluminium. However, it was also shown that the settlement characteristics of the sludges generated varied greatly depending on the metal being removed from solution.

To develop an understanding of the mechanisms involved in the formation of HDS, the formation of precipitates is considered and the impact of the Type II HDS process (see Section 2.13, i.e. mixing of recirculated sludge with metal solutions before adding pH) on the formation of the precipitates is reviewed. Sludges with good (synthetic zinc minewater) and poor (synthetic aluminium minewater) settlement characteristics are used to illustrate the extremes.

8.1 Metal ion precipitation and theory of nucleation

Classical nucleation theory (Walton, 1967), indicates that the two processes involved in the formation of precipitates from a saturated minewater are homogeneous nucleation (the generation of the precipitates in the bulk solution, i.e. in a single phase) and heterogeneous nucleation (the generation of the precipitates onto the surfaces of solid particles, i.e. between two phases).

Consider the precipitation of a metal hydroxide from a solution. The metal ions and hydroxyl ions are moving randomly through the solution. Depending on their concentrations, they can collide and combine to form a cluster (nucleus) of metal hydroxide, and depending on the free energy of the system, can form a thermodynamically more stable metal hydroxide precipitate (nucleation) or will re-dissolve and form separate metal and hydroxyl ions. The formation of the cluster of metal hydroxide will produce a solid/solution interface. Additionally, once the precipitate has formed, a shape change (rearrangement) may occur which also requires energy, however this 'strain energy' can be considered to be negligible. Therefore, the precipitation of metal hydroxide will depend on the metal and hydroxyl ion concentrations, the free energy that is available (the chemical driving force) and the energy required to form the interface (the interfacial energy).

Essentially, the free energy change (i.e. the free energy of formation ΔG) is energy gained from making the stable nucleus (ΔG_{bulk}) (which is always a negative contribution in a supersaturated solution) and the energy required to create a

surface (ΔG_{surf}) and is defined by Equation 8.1 (Stumm *et al.*, 1996).

$$\Delta G = \Delta G_{surf} + \Delta G_{bulk} \quad \text{(Equation 8.1)}$$

where:

ΔG = free energy of formation
ΔG_{surf} = work required to create a surface
ΔG_{bulk} = energy required to make bonds

Assuming that the interfacial energy is isotropic and the nucleus is assumed to be spherical, the free energy for formation of a nucleus of radius r may be written as presented in Equation 8.2 (Stumm, 1992).

$$\Delta G = 4\pi r^2 \sigma + 4/3\pi r^3 \Delta G_v \quad \text{(Equation 8.2)}$$

where:

ΔG = free energy of formation
r = radius of nucleus
σ = the interfacial energy per unit area of the nucleus (often call surface tension)
ΔG_v = the chemical driving force per unit volume of nucleus

Figure 8.1 shows the variation in the free energy of nucleation with increasing size of the nucleus.

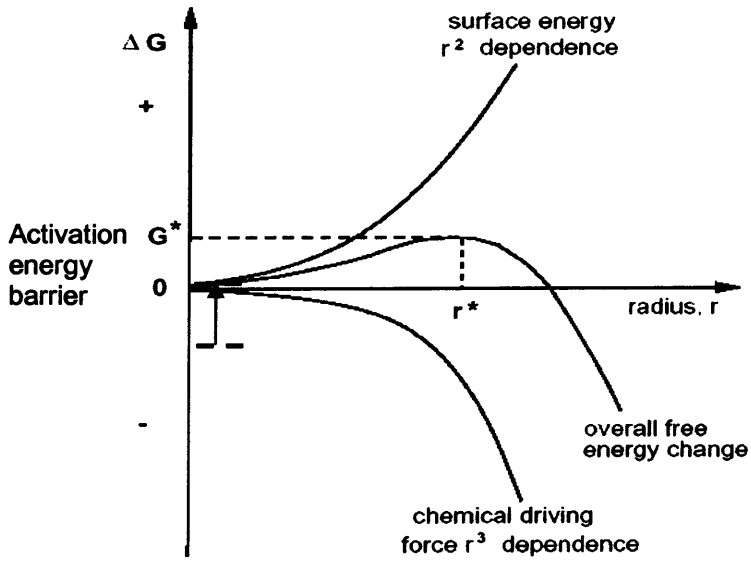


Figure 8.1: The free energy change associated with the formation of a nucleus as a function of radius r (modified from Stumm, 1992).

The nucleus will be viable (i.e. will grow rather than dissolve) when an increase in its size leads to a reduction in the overall free energy, this takes place at a critical radius r*. Below r*, the nucleus is not viable and will tend to dissolve back in to the

bulk solution. Above r* the nucleus (known as the critical nucleus, N*) is viable and will grow as an activation energy barrier for nucleation, ΔG^*, is exceeded.

Classical nucleation theory (e.g. Walton, 1967) also shows that as ΔG_v (the chemical driving force) is proportional to the saturation ratio, Ω (see Equation 8.3, Stumm, 1992; Walton, 1967), the free energy of formation will vary as the saturation ratio varies. Therefore, for ΔG^* to be exceeded, a critical degree of saturation (termed 'critical supersaturation') must also be exceeded before homogeneous nucleation can occur.

$$\Delta G_v = (KT/V) \ln \Omega \qquad \text{(Equation 8.3)}$$

where:

ΔG_v = the chemical driving force per unit volume of nucleus
T = temperature
K = Boltsmann constant
V = 'molecular' volume
Ω = the saturation ratio, i.e. $\frac{\text{concentration in solution}}{\text{concentration at saturation}}$

Presented in Figure 8.2 is a schematic representation of how the free energy of formation varies with saturation ratio (Stumm, 1992). This shows, that as the saturation ratio increases, ΔG^* decreases, therefore as the pH of a solution increases (and the saturation ratio increases), the activation barrier decreases and homogeneous nucleation is more likely.

Classical nucleation theory also shows that the rate at which a nuclei forms is dependant on the activation barrier energy, see Equation 8.4 (Walton, 1967; Stumm, 1992).

$$J = J_0 \exp(-\Delta G^*/kT) \qquad \text{(Equation 8.4)}$$

where:

J = the rate at which a nuclei is formed
J_0 = factor related to the efficiency of collisions of ions
T = temperature
K = Boltsmann constant
ΔG^* = the activation energy barrier

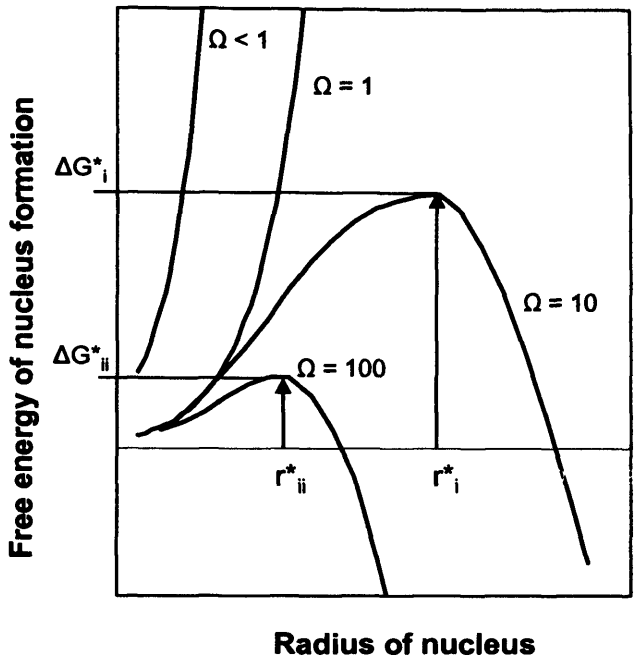


Figure 8.2: A schematic representation of the free energy of formation as a function of size, calculated for different saturation ratios (Stumm, 1992).

Considering Equations 8.3 and 8.4 it can be seen that the rate of nucleation is dependant on the saturation ratio. Figure 8.3 presents how the nucleation rate varies with the saturation ratio.

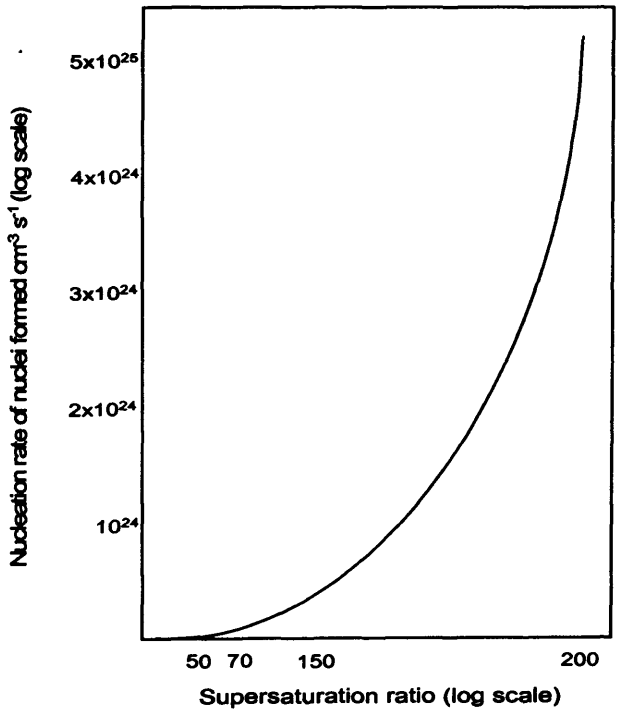


Figure 8.3: A schematic representation of nucleation rate versus saturation ratios (Stumm, 1992).

Equations 8.2, 8.3 and 8.4, show that the rate of homogenous nucleation can be seen to be controlled by the interfacial energy, the degree of supersaturation, the

collision frequency and the temperature.

Due to the rate of homogeneous nucleation being over 250 times the rate of heterogeneous nucleation, (Stumm, 1992) the formation of very small precipitates can occur with high degrees of supersaturation.

As with chemical reactions, where a catalyst reduces the activation energy, the presence of a solid substrate will reduce the activation energy barrier in heterogeneous nucleation. When there is a good 'match' between the precipitate to be formed and the solid substrate, surface-catalytic effects can occur, which can lower the interfacial energy. Presented in Figure 8.4 is the schematic representation of how a solid substrate can catalyze nucleation (Stumm, 1992). Due to the good match, the interfacial energy between the substrate and the precipitate will be lower than that between the precipitate and the bulk solution and nucleation is able to take place at lower degree of saturation.

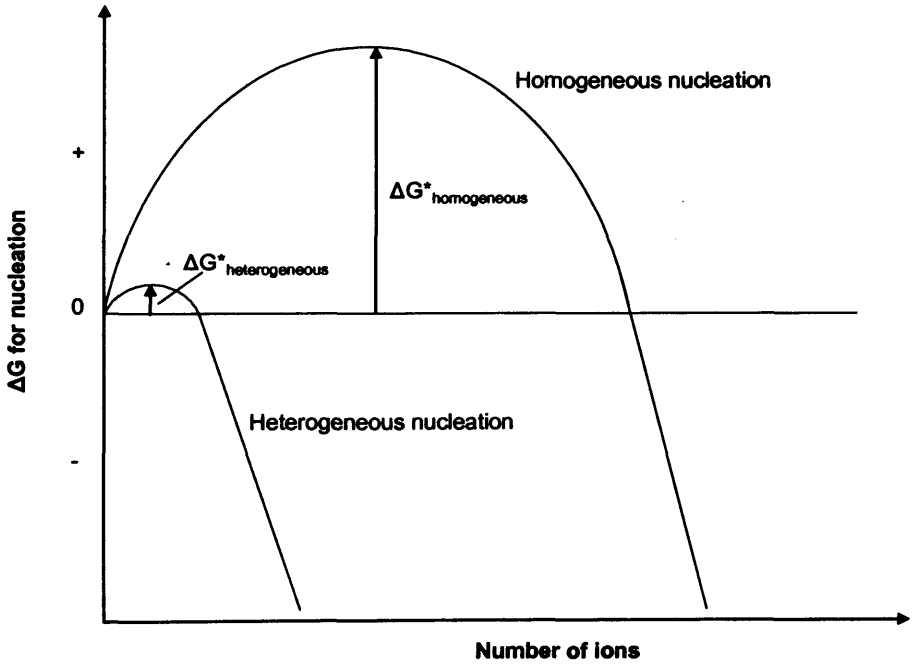


Figure 8.4: Schematic effect of substrate on nucleation (modified from Stumm, 1992).

The presence of the substrate will not only potentially encourage surface-catalytic effects but can also enhance nucleation by chemical and physical adsorption. However, certain cations, e.g. Mg^{2+}, can also retard the nucleation process due to slow water exchange rates compared to other bivalent ions (Stumm *et al.*, 1996). An example of this is the limited precipitation of calcite in seawater due to the Mg^{2+} inhibiting surface nucleation. This possible inhibitory effect of Mg^{2+} was seen during Batch Test 3 and Continuous Trial 5, when the formation of HDS was

retarded.

In summary, for precipitation of metal hydroxide to occur, the metal ions must first collide and combine with hydroxyl ions. An activation energy barrier for nucleation must be exceeded for the nucleus to be viable and once the activation energy barrier is exceeded nucleation can occur. If no substrate is present, homogeneous nucleation will dominate. The presence of a substrate can lower the activation energy barrier for nucleation and ensure that heterogeneous nucleation dominates.

8.2 Why are aluminium precipitates formed before zinc precipitates?

The classical solubility curves for the removal of metal hydroxides, such as presented in Figure 2.4, indicate that the metals used during this research would be removed from solution in the following order with increasing pH:

$Fe^{3+} < Al^{3+} < Zn^{2+} < Fe^{2+} < Mn^{2+}$.

When considering aluminium and zinc, it can be seen that aluminium is removed from solution at a lower pH (circa 6.8) than zinc (circa 9.0). The removal of metals from a mixed metal solution, when a single pH is used, can lead to varying degrees of supersaturation, and hence varying rates of precipitation.

Table 8.1 presents the changes in the energies of hydration (Martell *et al.*, 1996) for the metal ions reviewed during this research and follow a similar order as the classical solubility curves. The energies of hydration indicate that a more negative change occurs from the hydration of aluminium ions compared to the hydration of zinc ions, indicating that aluminium has a higher affinity to hydration than zinc.

Table 8.1: Energies of hydration (Martell *et al.*, 1996)

Ion	-ΔG (kcal/mol)	-ΔH(kcal/mol)	-ΔS(cal/deg/mol)
Mn^{2+}	437.8	459.2	72.1
Fe^{2+}	456.4	480.2	79.8
Zn^{2+}	484.6	506.8	74.5
Al^{3+}	1103.3	1141.0	126.6
Fe^{3+}	1035.5	1073.4	127.5
OH^-	90.6	101.2	35.6

Note:
The energies refer to the process (at 298.16 K) M^{n+} (g) → Mn^+ (aq), and are based on the convention that for the reaction H^+ (g) → H^+ (aq) – ΔG is 260.5 kcal/mol, and –ΔS is 31.3 cal/mol.

ΔG change in energy of formation
ΔH change in enthalpy of formation
ΔS change in entropy of formation

8.2.1 Metal ion hydration

In general, smaller metal ions can be hydrated more easily than larger ions due to electrostatic theory, hence a smaller ion, such as aluminium (see ionic radii, R_i, in Table 8.2, CRC Press, 2005), contains a more concentrated charge which can lead to a greater electrostatic interaction with water molecules (a detailed explanation can be found in the literature, e.g. Chang, 2000).

Table 8.2: Number of water molecules in inner and outer hydration spheres ((i) Martell *et al.*, 1996; (II) CRC Press, 2005)

Ion	N_P (i) (number)	N_T (i) (number)	R_i(ii) (Å)
Mn^{2+}	6	-	0.83
Fe^{2+}	6	10-13	0.61
Zn^{2+}	6	10-13	0.74
Al^{3+}	6	13	0.54
Fe^{3+}	6	-	0.55

where:
N_P = Water molecules in the inner (primary) hydration (coordination) sphere, the coordination number
N_T = Total number of water molecules, the hydration number
Ri = Ionic radius

When metal ions are in solution, they have a number of water molecules directly bound to them in the inner hydration sphere called the coordination number, and a number of water molecules loosely held in the outer hydration sphere. The total number of water molecules bound in the inner and outer spheres is called the hydration number. Therefore, different metal ions can be surrounded by different numbers of water molecules, which can exert different electrostatic charges. Also, as the metal ion moves, the bound water molecules also move with the metal ion and do not exhibit individual motion. The forces associated with water interactions will have to be overcome prior to nucleation occurring. Presented in Table 8.2 are the numbers of water molecules in the inner and outer hydration spheres. It can be seen that there is little difference between the number of water molecules in the hydration spheres for the metal ions reviewed.

For inner-sphere surface complexion to occur, through adsorption, an inner sphere water molecule must dissociate first. Therefore, if the rate at which water is lost is slow, adsorption will be slow. Figure 8.5 (Crumbliss *et al.*, 1988) shows the rate of water loss from common cations.

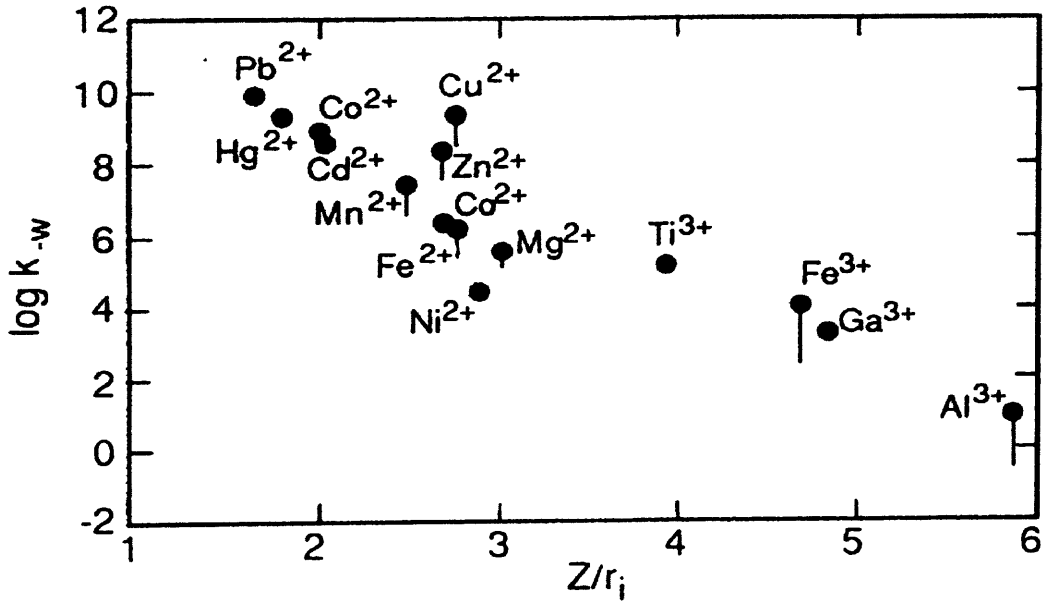


Figure 8.5: Rate of water loss from metal cations as a function of the ratio of the charge (Z) to the radius (r_i) of the metal ion (Crumbliss *et al.*, 1988).

Note: k_w is defined as the rate constant of water exchange

It can clearly be seen that Al^{3+} has a lower rate of water loss compared to Zn^{2+}, therefore Al^{3+} will potentially adsorb to the surface at a slower rate than Zn^{2+}. Additionally, as the Al^{3+} cation is adsorbed, the water molecules associated with

the Al^{3+} cation are potentially also removed from solution, due to the high electrostatic interactions between the Al^{3+} cation and the water molecules, resulting in a precipitate with high water content. However, due to the increased Zn^{2+} cation size resulting in less intense electrostatic forces, the associated water molecules are possibly released during nucleation resulting in a precipitate with lower water content.

8.3 Formation of precipitates during minewater treatment

To understand why the sludge generated from synthetic zinc and aluminium minewaters had different characteristics, the mechanisms involved in the formation of the metal hydroxide precipitates in conventional and Type II HDS minewater treatment are explored.

8.3.1 Formation of precipitates during conventional minewater treatment

In conventional minewater treatment (Figure 2.3), the sludge generated is subjected to a single pass process (Section 2.6), summarised as follows:

1. In the reactor, the pH of the minewater is changed to the required operating pH (dependant on the target metals to be removed) in one step. This change in pH increases the degree of supersaturation, making homogeneous nucleation likely.
2. The precipitates generated are flocculated, normally by the addition of an anionic polymer.
3. The precipitated solids are then settled, where a certain amount of self compression occurs, prior to the settled sludge being removed from the system.

Therefore, the mechanism for generating precipitates in conventional minewater treatment is: an increase in the degree of supersaturation due to the sudden rise in pH and precipitation dominated by homogeneous nucleation. The resulting sludge is generally of low solids concentration, typically below 5% w/w (see Section 2.6).

8.3.2 Formation of precipitates during Type II HDS treatment

In Type II HDS minewater treatment (Figure 2.13), the sludge generated is subjected to a repeated cyclic process, as described in Section 2.10, and

summarised as follows:

1. The incoming minewater is mixed with the recirculated sludge in the Stage I Reactor, where the majority of the dissolved metals are removed from solution (e.g. see Table 4.6 and Table 6.6).
2. The slurry output from the Stage I Reactor gravitates into the Stage II Reactor, where the target pH is maintained, normally by the addition of either $Ca(OH)_2$ or NaOH and the remainder of the dissolved metals are removed from solution.
3. The precipitates generated are flocculated, normally by the addition of an anionic polymer.
4. The precipitated solids are then settled, where a certain amount of self compression occurs, prior to some of the settled sludge being removed from the system and the rest returned to the Stage I Reactor.

In order to explore the predominant mechanisms at work in the formation of Type II HDS, it is useful to consider the specific process conditions in the reactors for both zinc (which forms HDS readily) and aluminium (which produced poor HDS) minewater solutions. Figure 8.6 presents the Type II HDS process conditions operated during Continuous Trial 2 (Section 6.5) when synthetic zinc minewater was used as the feed. The feed contained 154 mg/l of Zn^{2+} at a pH of approximately 6.8 (see Figure 6.19). Initially the pH in the Stage II Reactor was maintained at 7.5 using NaOH, with the recirculated solids capable of maintaining a pH of about 7.0 in the Stage I Reactor. At these conditions it was difficult to form sludge with suitable settlement characteristics, resulting in problems with the running of the continuous pilot plant (see Section 6.5.1). However, the results from the Batch Test 5 (Section 5.10), when synthetic zinc minewater was used as the feed, showed that Type II HDS could easily be formed from synthetic zinc minewater. Though Figure 5.43 would indicate comparable Stage I pH measurements, the precise operating conditions in this batch test need to be considered in detail before commenting on these apparent differences. In the zinc batch test, the incoming synthetic minewater (which had a pH of circa 4.0) was in fact contacted with sludge at a pH of 9.2 (as this was the final target pH of the zinc batch test), and as mixing continued, the resultant slurry pH dropped towards 6.0. This observation led to the decision to increase the Stage II Reactor pH during the

zinc continuous trial to 8.8 (on the 18th November 2003), which resulted in a stable pH of 8.5 in the Stage I Reactor. At this new operating condition there was a dramatic improvement in the sludge characteristics (see Figure 6.28).

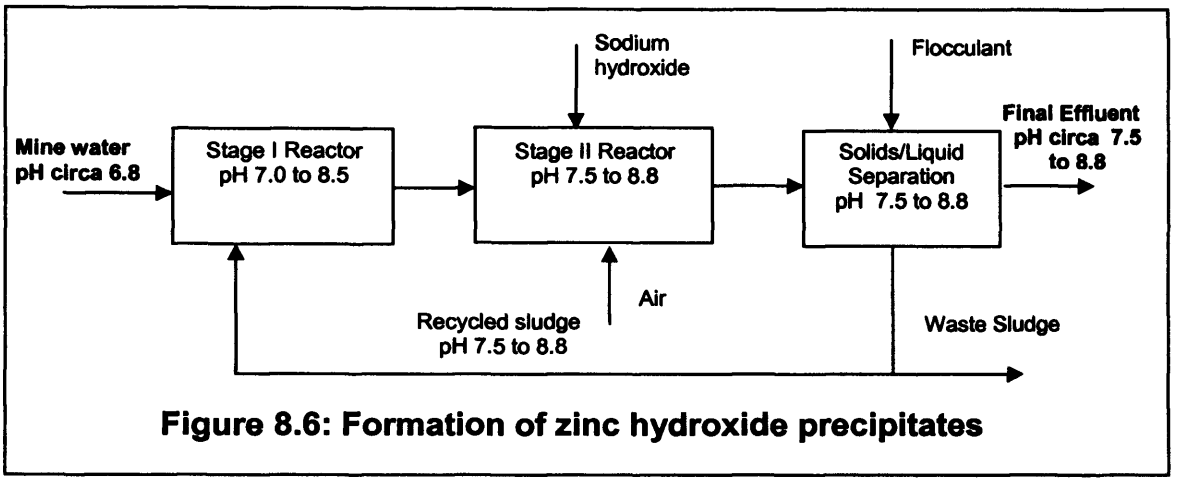


Figure 8.6: Formation of zinc hydroxide precipitates

It is now necessary to comment on the fate of a Zn^{2+} ion as it enters the Stage I Reactor. Previous discussions (see Section 8.1) have shown that both homogeneous and heterogeneous nucleation is possible. The homogeneous behaviour will dominate if the OH^- concentration is high (see Section 8.1), however the more advantageous heterogeneous behaviour will be favoured if the Zn^{2+} ions are attracted to the solid surfaces present (i.e. recirculated sludge) rather than nucleating in the bulk solution (see Section 8.1). Such adsorption will occur by chemical and physical mechanisms. The author has not been able to find data for chemisorption of Zn^{2+} onto zinc hydroxide, though it is considered that chemisorption will be occurring to some extent. In considering the physical adsorption, the electrostatic interactions need to be considered, see Section 7.4.1. Clearly, if the solid is net negatively charged the zinc cation adsorption will be easier. Figure 7.9 shows that the 'young' sludge PZC is near to a pH of 8.1. This leads to the conclusion that, during the early stages of the continuous trial for formation of HDS from synthetic zinc minewater solutions, the recirculated particles were net positive and electrostatic repulsion occurred between the cations and the surfaces. It is also the case that particles in the Stage II Reactor during the early stages were also net positive. Once the pH was raised to 8.75, the stable pH in Stage I Reactor reached 8.5 and at this operating condition the particles were net negative in both Stage Reactors and consequently HDS was readily formed. This suggests a very strong link between the need for significant physical adsorption in the Stage I Reactor for the formation of Type II HDS.

It is worth noting that as the sludge aged during the zinc continuous trial the PZC dropped and the zeta potential became more negative at the stable pH, increasing the attraction between the recirculated solids and the metal cations.

However, if the pH in Stage I Reactor was excessively high (and increasing the degree of supersaturation), it is likely that the balance between surface adsorption and homogeneous nucleation would shift towards the latter and result in poorer HDS being formed. This was not tested specifically in the present research since the attention was focused on generation of Type II HDS. It would be interesting to explore this hypothesis in more detail since it suggests an enhanced performance in the Type II HDS process as compared to the Type I HDS process.

As a comparison to the process conditions presented in Figure 8.6, when HDS was formed from synthetic zinc minewater solutions, Figure 8.7 presents the process conditions when Type II HDS was formed from synthetic aluminium minewater solution during Continuous Trial 3 (see Section 6.6). During this trial the feed contained 143 mg/l of Al^{3+} at a pH of approximately 3.0.

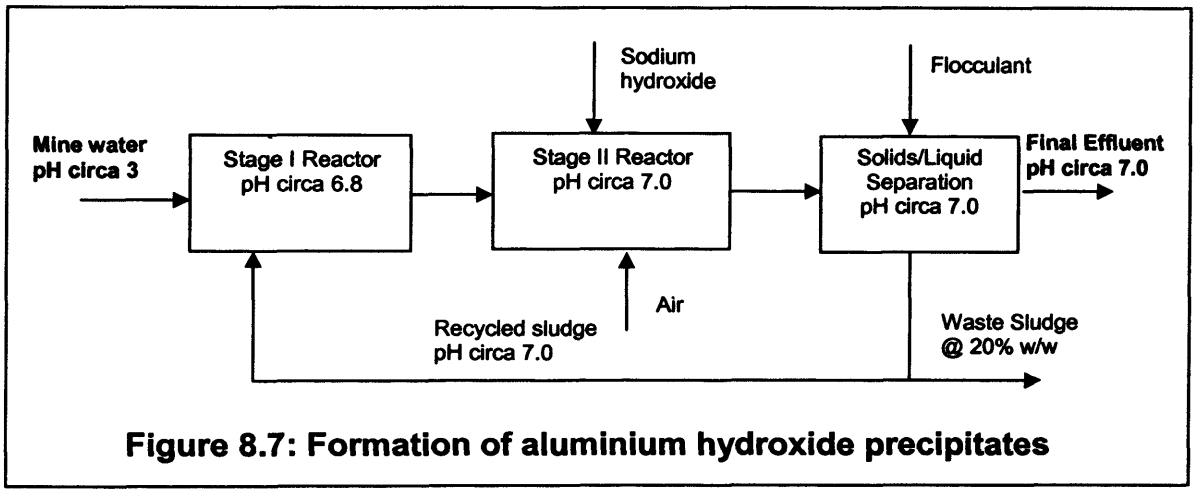


Figure 8.7: Formation of aluminium hydroxide precipitates

Initially the pH in the Stage II Reactor was maintained at 6.0 using NaOH, with the resulting recirculated sludge maintaining a pH of about 5.0 in the Stage I Reactor. As with the continuous zinc trial, the process conditions during the initial stages of the continuous aluminium trial made it difficult to form HDS with good settling characteristics. However, the results from Batch Test 6 showed that HDS can be formed from synthetic minewater where Al^{3+} is the dominant ion. As with the zinc batch test conditions, the mixing of the sludge with the synthetic minewater in the aluminium batch test resulted in the pH dropping from an initial 9.2 to a much lower pH of circa 5.5. Due to the observations made during the aluminium batch

test, and the experiences gained during the continuous zinc trial, it was decided to increase the Stage II Reactor pH to 6.9 (on the 8th December 2003), which resulted in a pH of 6.75 in the Stage I Reactor. At these new operating pHs there was an improvement in the sludge characteristics (see Figure 6.40).

As discussed with the synthetic zinc minewater work, homogeneous behaviour will dominate if the OH^- concentration is high, whilst the more advantageous heterogeneous behaviour will be favoured if the Al^{3+} ions are attracted to the solid surfaces present (i.e. recirculated sludge) rather than nucleating in the bulk solution. Figure 7.10 shows that the 'young' sludge PZC is near to a pH of 8.75. It can therefore be concluded that, as with the zinc trial, during the early stages of the continuous aluminium trial the formation of Type II HDS from synthetic aluminium minewater solutions the recirculated particles were net positive and electrostatic repulsion would occur between the cations and the surfaces. This was also the case in the Stage II Reactor when the sludge that particles were also net positive during the early stages of the trial.

Once the pH was raised to 6.9, the stable pH in Stage I reached 6.75, which is just above the PZC for the 'old' sludge (see Figure 7.10) which is near to a pH of 6.6, hence at this new operating condition the particles were net negative in both Stage Reactors and Type II HDS was able formed. This confirms the link between the need for significant physical adsorption in the Stage I Reactor and the formation of Type II HDS.

Figure 6.39 shows that during the initial stages of the trial there was no improvement in the settlement velocity characteristics, i.e. there is no movement from left to right in the settling characteristics. However, after day 9 of the continuous aluminium trial, when the Stage II Reactor operating pH was increased, there is a clear improvement in the settlement velocity, i.e. an increased movement from left to right for the grouped settling characteristics. This confirms the assumption made in Section 6.10.3 by the author, that once the Stage I Reactor pH is stabilised, the operating conditions (see Table 6.34) are conducive for the generation of HDS by the Type II HDS process.

8.4 The formation of Type II HDS

Considering the observations made during both the batch tests and continuous trials (see Section 8.3), it is suggested that the mechanisms involved in the

formation of Type II HDS are as follows:

1. The mixing of the recirculated solids with the minewater prior to the addition of the alkali reagent ensures that the removal of the dissolved metals from solution is dominated by heterogeneous nucleation, and reduces the likelihood of homogeneous nucleation occurring. The recirculated solids not only act as a substrate for the nucleation of fresh precipitates but also limit the degree of saturation, hence limiting the nucleation rate, which further increases the likelihood of heterogeneous rather than homogeneous nucleation occurring. Heterogeneous nucleation is enhanced further by:
    a. An increased collision frequency due to the presence of high concentrations of recirculated solids.
    b. The negative zeta potential of the recirculated solids causes the positively charged metals to be electrostatically adsorbed to the surface of the negatively charged recirculated solids.
    c. The good 'match' between the nucleus being formed and the recirculated solids encourages surface-catalytic effects, lowering the interfacial energy and hence lowering the energy barrier of nucleation and allowing the dissolved metals to be removed at lower degrees of saturation.
2. Due to the increase in the pH in the Stage II Reactor as a result of the alkali addition, the adsorbed metals are precipitated as metal hydroxides on the solid present. The increase in the pH also completes the removal of the dissolved metals and ensures the solids present have a zeta potential that is highly negative. The recirculated negatively charged solids encourage electrostatic adsorption of the fresh metals in the Stage I Reactor.

In summary, it can be seen that mixing the recirculation sludge with the minewater ensures heterogeneous nucleation will dominate. The positive metal cations adsorb, through electrostatic adsorption, to the surface of the negatively charged recirculated solids in the Stage I Reactor and, following the addition of the alkali in the Stage II Reactor, the metal cations are precipitated in the solid as metal hydroxides.

It can be seen that there is a conflict between the need for high pH for a large negative zeta potential for immobilisation of the metal cation by electrostatic adsorption, and lower pH in order to reduce homogeneous nucleation reactions.

9 CONCLUSIONS

The first full-scale HDS treatment plant was installed at Bethlehem Steel works (Kostenbader, 1970). However, though numerous other HDS treatment plants have been installed worldwide, and the knowledge of the HDS process as a whole has increased greatly, the detailed scientific understanding of the key parameters has not been reported in the literature.

Kostenbader (1970) and Bosman (1983) suggested that the key process parameters included:

- Total iron content of the acid minewater;
- Fe (II) to Fe (III) iron ratios in the feed water i.e. oxidation state of the minewater;
- Ratio of solids recirculated to new solids precipitated;
- Point of alkalinity addition;
- Operating pH; and
- Amount of calcium sulphate precipitated from solution.

These are still reported as key to the formation of HDS, though no detailed scientific explanation has been reported in the literature as to why and how these parameters affect the formation of HDS.

The research undertaken for this thesis has attempted to move the scientific understanding of the HDS process, and in particular the Type II HDS process, forward and dispel some misconceptions and contradictory beliefs surrounding the HDS process.

From the research undertaken, and presented in this thesis, the following conclusions can be drawn:

1 HDS can be formed using non calcium based alkali reagents, e.g. sodium hydroxide and sodium carbonate. The presence of carbonates (Aubé *et al.*, 1997) and gypsum (Bosman, 1983) are not required in the formation of HDS, though their presence may help with the initial formation of HDS.

2 There is no requirement for iron to be present in the formation of HDS (Bosman, 1983). HDS with better settling and dewatering characteristics

was formed from synthetic zinc and manganese minewater compared to synthetic iron minewater.

3 The HDS generated from synthetic zinc (a bivalent metal) minewater settled faster and to a smaller sludge volume than the HDS generated from both synthetic aluminium and iron (trivalent metals) minewaters. It is therefore suggested that the valence of the metal removed does not affect the HDS process. It is also concluded that the Fe (II) to Fe (III) iron ratios in the feed water (Kostenbader *et al.*, 1970; Bosman, 1983), i.e. oxidation state of the minewater, is not critical to the formation of HDS as sludge with better settling and dewatering characteristics was formed from synthetic zinc and manganese minewaters than from synthetic iron minewater with high Fe (II) concentrations.

4 HDS with good settling and dewatering characteristics can be formed by Type I and Type II HDS processes providing good process control is maintained and the correct sequence of inputs is followed.

5 It would appear that the level of crystalinity does not affect the settling and dewatering characteristics of HDS formed. Sludge with poor degrees of crystalinity was detected by XRD analysis, and the SEM and TEM analysis undertaken indicated that the HDS is an aggregation of floc precipitates. HDS may contain very small (nano crystals), as suggested in the literature, however this requires further investigation.

6 The time it takes to form HDS, as shown by continuous Trial 6 (mixed metals), is minewater specific with each minewater requiring subtly different operating process parameters (e.g. mass recirculation rates, see Section 6.10.3). The Stage I Reactor solids to new solids formed ratio, which can also be derived from the mass recirculation ratio, is key to the formation of HDS.

7 The research undertaken would indicate that the surface chemistry and surface interactions, controlled by the Stage I Reactor solids to solids formed ratio, is fundamental to the formation of HDS. Operating the Stage I Reactor at a pH in excess of the point of zero charge appeared to enhance the formation of HDS.

8 The presence of other species, e.g. calcium and magnesium cations, can 'swamp' the process and slow down the formation of HDS they do not prevent the formation of HDS. This was confirmed by the formation HDS from synthetic iron in seawater minewater (containing saline waters with high concentrations of calcium).

9 The HDS process greatly enhances the sludge dewatering characteristics of the sludge generated during minewater treatment.

10 The dominant mechanism for the formation of Type II HDS involves establishing a pH in the Stage I Reactor that gives a negative charge to the recirculated solids. Physical adsorption then ensures heterogeneous nucleation. Control of the pH in the Stage II Reactor ensures removal of the final trace of metals from solution and return of sludge that is capable of achieving the desired pH in the Stage I Reactor. A review of the relevant literature suggests that too high a pH in the Stage I Reactor will favour homogeneous nucleation and hence inhibit HDS formation.

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